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(54) ORGANIC/INORGANIC COMPOSITE GRADIENT MATERIAL, AND ITS PREPARATION AND USE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an organic/inorganic composite gradient material whose composition continuously varies in the thickness direction and which is useful in various applications as a new functional material.

SOLUTION: An organic/inorganic composite gradient material comprises a composite in which an organic polymer compound and a metallic compound have been chemically bonded and has a structure in which the content of the metallic compound continuously varies in the direction from the depth of the material to its surface. A method of preparing the organic/inorganic composite gradient material comprises forming a coated film composed of a specific organic/inorganic composite film-forming coating solution on an organic substrate and drying the resulting film with heating. A film-forming coating material is composed of the organic/inorganic composite gradient material. An article is coated with the film-forming coating material.

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CLAIMS

[Claim(s)]

[Claim 1] The organic-inorganic compound inclination ingredient with which it is organic-inorganic composite material containing the chemical bond object of an organic high molecular compound and a metal system compound, and content of the metal system compound in an ingredient is characterized by having the component inclination structure of changing in the depth direction from the front face of an ingredient continuously.

[Claim 2] The organic-inorganic compound inclination ingredient according to claim 1 which is what organic-inorganic composite material becomes from the chemical bond object of an organic high molecular compound and a metal system compound.

[Claim 3] The organic-inorganic compound inclination ingredient according to claim 1 or 2 whose metal system compound is a metallic-oxide system compound.

[Claim 4] The organic-inorganic compound inclination ingredient according to claim 1 or 2 whose metal system compound is a metal nitride system compound which comes to carry out a chemical bond to an organic high molecular compound through a metallic-oxide system compound.

[Claim 5] An organic-inorganic compound inclination ingredient given in any 1 term of claims 1-4 whose thickness is 5 micrometers or less.

[Claim 6] The organic-inorganic compound inclination ingredient according to claim 3 or 5 which is the thing to which the chemical bond object of an organic high molecular compound and a metal system compound comes to carry out hydrolysis processing of the mixture of the organic high molecular compound which has in a molecule the metal content radical which can be combined with a metallic oxide by hydrolysis, and the metallic compounds which can form a metallic oxide by hydrolysis.

[Claim 7] The organic-inorganic compound inclination ingredient according to claim 4 or 5 with which the chemical bond object of an organic high molecular compound and a metal system compound comes to carry out hydrolysis processing of the organic high molecular compound which has in a molecule the metal content radical which can be combined with a metal nitride polymer by hydrolysis, and the mixture with a metal nitride polymer.

[Claim 8] The organic high molecular compound which has in a molecule the metal content radical which can be combined with a metallic oxide or a metal nitride polymer by hydrolysis is copolymerization or the organic-inorganic compound inclination ingredient according to claim 6 or 7 which is made to carry out condensation polymerization and is obtained about the monomer which has the above-mentioned metal content radical, and the monomer which does not contain a metal.

[Claim 9] The organic-inorganic compound inclination ingredient according to claim 8 whose organic high molecular compound which has in a molecule the metal content radical which can be combined with a metallic oxide or a metal nitride polymer by hydrolysis is the copolymer of the monomer which has an ethylene nature partial saturation radical, and the monomer containing an ethylene nature partial saturation radical and the above-mentioned metal content radical.

[Claim 10] The organic-inorganic compound inclination ingredient according to claim 6 whose metallic compounds which can form a metallic oxide by hydrolysis are metal alkoxides.

[Claim 11] An organic-inorganic compound inclination ingredient given in any 1 term of claims 1-10 whose fields which consisted of a filmy material formed on the organic base material, and are in contact with the organic base material of this filmy material on parenchyma are organic macromolecule system compound components and another open system sides of whose are metal system compound components.

[Claim 12] (A) The organic high molecular compound which has in a molecule the metal content radical which can be combined with a metallic oxide or a metal nitride polymer by hydrolysis, and the metallic compounds which can form a metallic oxide by (B) (b) hydrolysis, Or after [which does not carry out hydrolysis processing of the mixture with a (b) metal nitride polymer] carrying out [a ** or] hydrolysis processing and preparing coating liquid, The manufacture approach of an organic-inorganic compound inclination ingredient given in any 1 term of claims 1-4 characterized by forming the paint film which consists of the above-mentioned coating liquid on the substrate which consists of organic material, and subsequently carrying out stoving processing.

[Claim 13] The approach according to claim 12 the thickness of a dry paint film is 5 micrometers or less.

[Claim 14] (A) The organic high molecular compound which has the metal content radical which can be combined with a metallic oxide or a metal nitride polymer by hydrolysis in the molecule of a component is copolymerization or the approach according to claim 12 or 13 which is made to carry out condensation polymerization and is acquired about the monomer which has the above-mentioned metal content radical, and the monomer which does not contain a metal.

[Claim 15] (A) An approach given in any 1 term of claims 12-14 whose organic high molecular compounds which have the metal content radical which can be combined with a metallic oxide or a metal nitride polymer by hydrolysis in the molecule of a component are the copolymers of the monomer which has an ethylene nature partial saturation radical, and the monomer containing an ethylene nature partial saturation radical and the above-mentioned metal content radical.

[Claim 16] (B) Approach given in any 1 term of claims 12-15 whose metallic compounds which can form a metallic oxide by hydrolysis of a (b) component are metal alkoxides.

[Claim 17] The coating agent characterized by making the coat which becomes claim 1 thru/or any 1 term of 11 from the organic-inorganic compound inclination ingredient of a publication form on a base material.

[Claim 18] (A) The coating agent according to claim 17 which consists of coating liquid which does not carry out hydrolysis processing of the organic high molecular compound which has in a molecule the metal content radical which can be combined with a metallic oxide or a metal nitride polymer by hydrolysis, the metallic compounds which can form a metallic oxide by (B) (b) hydrolysis, or the mixture with a (b) metal nitride polymer, and which was obtained [the ** or] by carrying out hydrolysis

processing.

[Claim 19] The coating agent according to claim 17 or 18 used as an object for paint film formation to an organic base material.

[Claim 20] The coating agent according to claim 17 or 18 used as adhesives with an organic material, inorganic, or a metallic material.

[Claim 21] The coating agent according to claim 17 or 18 used as an object for interlayer formation made to intervene between an organic base material and the coat layer which contains an inorganic system or a metal system ingredient at least.

[Claim 22] The coating agent according to claim 21 whose coat layer which contains an inorganic system or a metal system ingredient at least is a photocatalyst activity ingredient layer.

[Claim 23] The coating agent according to claim 21 whose coat layer which contains an inorganic system or a metal system ingredient at least is an inorganic system or a metal system conductivity ingredient layer.

[Claim 24] The coating agent according to claim 21 which is the rebound ace court layer in which the coat layer which contains an inorganic system or a metal system ingredient at least contains an inorganic system or a metal system ingredient.

[Claim 25] The coating agent according to claim 21 whose coat layer which contains an inorganic system or a metal system ingredient at least is an inorganic system, a metal system material-for-optical-recording layer, an inorganic system, or a metal system dielectric layer.

[Claim 26] The coating agent according to claim 17 or 18 used as an object for interlayer formation made to be placed between front faces between the metal system base materials and photocatalyst activity ingredient layers which have an organic system paint film.

[Claim 27] The coating agent according to claim 22 or 26 whose photocatalyst activity ingredient layer is the titanium-dioxide coating film.

[Claim 28] The base material characterized by using the organic-inorganic compound inclination ingredient of a publication for claim 1 thru/or any 1 term of 11.

[Claim 29] The base material according to claim 28 which is an organic base material.

[Claim 30] The base material according to claim 29 which is what has the coat layer in which an organic base material makes an organic-inorganic compound inclination ingredient placed between as an interlayer, and contains an inorganic system or a metal system ingredient at least.

[Claim 31] The base material according to claim 28 which is a metal system base material which an organic-inorganic compound inclination ingredient is made to intervene as an interlayer, and has a photocatalyst activity ingredient layer, and with which an organic system paint film is prepared in a front face.

[Claim 32] The charge of organic - inorganic binder characterized by using the organic-inorganic compound inclination ingredient of a publication for claim 1 thru/or any 1 term of 11 as adhesives.

[Claim 33] Goods characterized by having the coat layer which the organic-inorganic compound inclination ingredient of a publication is made placed between claim 1 thru/or any 1 term of 11 as an interlayer, and contains an inorganic system or a metal system ingredient at least.

[Claim 34] Goods according to claim 33 whose coat layer which contains an inorganic system or a metal system ingredient at least is a photocatalyst activity ingredient layer.

[Claim 35] Goods according to claim 33 whose coat layer which contains an inorganic system or a metal system ingredient at least is an inorganic system or a metal system conductivity ingredient layer.

[Claim 36] Goods according to claim 33 which are the rebound ace court layers in which the coat layer which contains an inorganic system or a metal system ingredient at least contains an inorganic system or a metal system ingredient.

[Claim 37] Goods according to claim 33 whose coat layer which contains an inorganic system or a metal system ingredient at least is an inorganic system, a metal system material-for-optical-recording layer, an inorganic system, or a metal system dielectric layer.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the application of a new organic-inorganic compound inclination ingredient, its manufacture approach, and this inclination ingredient. This invention is organic-inorganic composite material containing the chemical bond object of an organic high molecular compound and a metal system compound in more detail. It has the component inclination structure where the content of this metal system compound changes in the thickness direction of an ingredient continuously. An organic-inorganic compound inclination ingredient useful for various applications as high-performance material, the coating agent for coat formation which becomes the approach list which manufactures this thing efficiently from this inclination ingredient. For example, it is related with the base material and goods which used the coating agent and this inclination ingredient which are used as an object for interlayers made to intervene between adhesives with a paint film, an organic material, inorganic, or a metallic material and an organic base material, an inorganic system, or a metal system ingredient layer.

[0002]

[Description of the Prior Art] It becomes difficult to make it satisfied with a single high molecular compound in recent years with diversification of the demand about the engine performance of organic polymeric materials and a function, and adding and compound-izing a dissimilar material with a property which is different in a high molecular compound is performed. For example, physical-properties reforming by distributing reinforcement in organic polymeric materials is performed widely, the inorganic filler of the shape of powder, such as organic [, such as a carbon fiber, a glass fiber, a metal fiber, ceramic fiber, and an aramid fiber,], an inorganic fibrous material or a calcium carbonate, a silica, and an alumina, etc. is added, and, specifically, distributing homogeneity is performed. Moreover, research which makes a new function discover is also briskly done by mixing a high molecular compound of a different kind, making it compatibility-ize through a compatibilizer by the case, and polymer-alloy-izing.

[0003] On the other hand, the metal-ceramic compound functionally gradient material for which the presentation of an ingredient is changed little by little and the functionally gradient material which is the composite material with which properties completely differ on a table and the reverse side attracts attention for example, which has the thermal resistance of the ceramics and metalead reinforcement is developed as an airframe ingredient of a supersonic transport etc. recently.

[0004] Such a functionally gradient material is classified into an inorganic inclination ingredient, an organic inclination ingredient, and an organic-inorganic compound inclination ingredient. By controlling the distribution density which mixes two or more ingredients, for example, two or more inorganic materials of a different kind, two or more organic materials of a different kind or one or more sorts of organic materials, and one or more sorts of inorganic materials, and changes with locations, orientation, etc. From making the physical properties of two or more component ingredients discover, and getting, space and the aeronautical-navigation field, the automobile field, the electronics field, the medical field, the energy field, and use [in / a radiation, the shielding field of an electromagnetic wave, etc. / further] are expected, for example.

[0005] by the way, the so-called Honda-Fujishima effectiveness ["an industrial-chemistry magazine" by which the photolysis of the water is carried out to hydrogen and oxygen by making semi-conductors, such as a titanium dioxide, into a photoelectrical pole — since the 72nd volume, and the 108th — 113-page (1969)] were found out, development and utilization research of a photocatalyst have come to be done briskly. If semi-conductor particles, such as a titanium dioxide, are excited with the light of the energy more than that band gap, an electron will arise in a conduction band, and an electron hole will be generated in a valence band, and this photocatalyst will be rich in this energy, and will use an electronic-electron hole pair.

[0006] Such a photocatalyst is applied, for example, deodorization, antifouling, antibacterial, sterilization, decomposition, removal of the various matter which poses a problem on the environmental pollution in waste water and waste gas further, etc. are considered. Although metallic sulfide, such as metallic oxides, such as the compound which has the semi-conductor-property of former versatility as a photocatalyst, for example, a titanium dioxide, an iron oxide, tungstic oxide, and a zinc oxide, a cadmium sulfide, and zinc sulfide, etc. is known, the titanium dioxide, especially the anatase mold titanium dioxide are useful as a practical photocatalyst in these. This titanium dioxide shows the photocatalyst activity which was excellent by absorbing the light of the specific wavelength of the ultraviolet-rays field included in everyday light, such as sunlight, and demonstrates functions, such as antifouling, deodorization, antibacterial, air cleaning, water purification, and a super-hydrophilic property, by the powerful oxidation originating in this photocatalyst operation.

[0007] Such a photocatalyst function that photocatalysts, such as a titanium dioxide, have is demonstrated effectively, and research which uses it industrially is done briskly now. For example, it will be possible to give the operation which disassembles the organic substance into an ingredient front face only by irradiating light, and it will be begun to put dirt in practical use with pile glass, a tile, a toilet bowl, etc., if a photocatalyst is covered on the surface of an ingredient or is made to mix into the paint film on the front face of an ingredient. Moreover, development research of the various functional products using this photocatalyst is performed positively. the building materials which disassemble the nitrogen oxides used as the ringleader of (1) air pollution with solar light energy and (2), while carrying out spontaneous decomposition of the adhering dirt which comes to cover a glass front face with a transparent photocatalyst [for example,] Come to prepare a photocatalyst layer in a film front face using the super-hydrophilic property and antifouling property ability of glass and (3) photocatalysts which have antibacterial effectiveness. Utilization of the agent for waste water treatment which comes to cover titanium-dioxide impalpable powder to the window film stuck on side front front faces, such as a glass window, and (4) silica-gel particle is considered.

[0008] However, photocatalysts, such as a titanium dioxide with a photocatalyst function, are not simply supported to organic

substrates, such as plastics, but need a certain binder in many cases. Moreover, if this photocatalyst is directly coated on an organic substrate or is made to mix into this base material, the problem which says that it does not escape that an organic substrate deteriorates according to a photocatalyst operation for a short time will arise.

[0009] Although to prepare the coating film of photocatalysts, such as a titanium dioxide, through organic system adhesives etc. on an organic substrate in order to solve such a problem is also tried, the adhesive property of a binder and a photocatalyst object falls with time in this case, or the situation which is not desirable as for generating of nebula-izing and the interference color etc. is invited. Moreover, although to prepare the coating film of photocatalysts, such as a titanium dioxide, through inorganic system adhesives etc., for example on an organic substrate is also tried, in this case, an adhesive property with a substrate is not enough, or a crack etc. occurs in the glue line itself gradually, and the situation which is not desirable as for an adhesive fall with a binder and a base with time as a result, generating of nebula-izing and the interference color, etc. is invited. Moreover, to develop the microcapsule which covered photocatalysts, such as a titanium dioxide, with the silica, to mix this microcapsule into an organic base, and to give deodorization and an antibacterial function is tried. Since a photocatalyst cannot expose such a microcapsule to a front face easily, many minute holes exist in the capsule and the small organic substance of a molecule can enter while degradation of an organic substrate is controlled, a catalyst function is demonstrated effectively. However, it is also difficult for the microcapsule of such structure to make the photocatalyst activity into high activity, and it is difficult to fully apply the hydrophilization phenomenon which is another description of a photocatalyst. Moreover, complicated actuation is needed for the manufacture approach, and it has the fault of not escaping a manufacturing cost costing dearly.

[0010] On the other hand, the layer which consists of various inorganic systems or metal system ingredients other than said photocatalyst activity ingredient, for example, a conductive ingredient, a rebound ace court agent, material for optical recording, magnetic powder, an infrared absorption ingredient, etc. is prepared on a plastics base material, and producing high-performance material is performed widely. Since adhesion with a base material is generally inadequate when preparing such an inorganic system or a metal system ingredient layer on a plastics base material, an inorganic system primer layer is prepared on a plastics base material, and the method of making an inorganic system or a metal system ingredient layer form on it is used well. However, in this approach, although the adhesion with an inorganic system primer layer, an inorganic system, or a metal system ingredient layer was good, the adhesion of a plastics base material and an inorganic system primer layer had the problem of it being inferior to heat-resistant adhesion, or adhesion falling by the passage of time rather than was necessarily enough. Therefore, development of the technique of making an inorganic system or a metal system ingredient layer forming with sufficient adhesion on a plastics base material was desired.

[0011]

[Problem(s) to be Solved by the Invention] This invention is the basis of such a situation. The new various applications as high-performance material, For example, it is prepared between a paint film, and an organic material, inorganic or adhesives with a metallic material, an organic base material and a photocatalyst paint film. For applications, such as an interlayer which prevents degradation of an organic base material, and an interlayer which raises adhesion with an organic base material, an inorganic system, or a metal system ingredient layer, [useful] A presentation aims at offering the method of manufacturing efficiently the organic-inorganic compound inclination ingredient which changes continuously, and this thing, and its application in the thickness direction.

[0012]

[Means for Solving the Problem] The organic high molecular compound which has the metal content radical which can be combined with a metallic oxide or a metal nitride polymer by hydrolysis in a molecule as a result of repeating research wholeheartedly, in order that this invention persons may attain said purpose, and the metallic compounds which can form a metallic oxide by hydrolysis. Or the coating liquid which does not carry out hydrolysis processing of the mixture with a metal nitride polymer and which was obtained [the ** or] by carrying out hydrolysis processing is applied on an organic substrate. Organic-inorganic composite material containing the chemical bond object of the organic high molecular compound and metal system compound which are formed by carrying out stoving processing The content of the metal system compound in an ingredient is the new organic-inorganic compound inclination ingredient which has the component inclination structure of changing in the depth direction from the front face of an ingredient continuously, and it came to complete this invention for it being useful for said application based on a header and this knowledge.

[0013] Namely, this invention is organic-inorganic composite material containing the chemical bond object of (1) organic high molecular compound and a metal system compound. The organic-inorganic compound inclination ingredient with which content of the metal system compound in an ingredient is characterized by having the component inclination structure of changing in the depth direction from the front face of an ingredient continuously, (2) The coating agent characterized by making the coat which consists of the above-mentioned organic-inorganic compound inclination ingredient form on a base material, The coating agent used as an object for interlayer formation made to intervene preferably between the object for paint film formation and organic material to an organic base material, inorganic or the object for adhesives with a metallic material and an organic base material, and the coat layer that contains an inorganic system or a metal system ingredient at least, (3) The base material characterized by using the above-mentioned organic-inorganic compound inclination ingredient, (4) The charge of organic - inorganic binder characterized by using the above-mentioned organic-inorganic compound inclination ingredient as adhesives, And the goods characterized by having the coat layer which a (5) above-mentioned organic-inorganic compound inclination ingredient is made to intervene as an interlayer, and contains an inorganic system or a metal system ingredient at least are offered.

[0014] Moreover, the organic high molecular compound which has the metal content radical which can be combined with a metallic oxide or a metal nitride polymer by hydrolysis in the (A) molecule if said organic-inorganic compound inclination ingredient follows this invention and metallic compounds which can form a metallic oxide by (B) (b) hydrolysis, Or after [which does not carry out hydrolysis processing of the mixture with a (b) metal nitride polymer] carrying out [a ** or] hydrolysis processing and preparing coating liquid, the paint film which consists of the above-mentioned coating liquid can be formed on the substrate which consists of organic material, and it can manufacture by subsequently carrying out stoving processing.

[0015]

[Embodiment of the Invention] The organic - inorganic compound inclination ingredient of this invention has the component inclination structure of an organic high molecular compound and a metal system compound being organic-inorganic composite material containing the complex which comes to carry out a chemical bond, and organic - inorganic composite material which consists of this complex preferably, and changing continuously [the content of the metal system compound in an ingredient] from an ingredient front face to the depth direction.

[0016] The check of such component inclination structure can be performed by performing sputtering to the paint film front face of

an organic-inorganic compound inclination ingredient prepared on the substrate which consists for example, of organic material, shaving the film on it, and measuring the content of the carbon atom on the front face of the film, and a metal atom by X-ray photoelectron spectroscopy etc. with time on it. If an example is given and explained concretely, drawing 1 will be set in the below-mentioned example 1. Organic - inorganic composite material with a thickness of 0.6 micrometers prepared on the polymethylmethacrylate substrate (as a metal atom) Although the paint film front face before performing sputtering is occupied by the silicon atom about about 100% as been the graph which shows relation with the content of the sputtering time amount in the paint film which becomes including a silicon atom, a carbon atom, and a silicon atom and shown in this drawing While the film follows on being deleted by sputtering and the content of the silicon atom on the front face of the film decreases, the content of a carbon atom increases and a film front face serves as only a carbon atom from the time of sputtering time amount passing over for about 30 minutes mostly.

[0017] That is, in this inclination ingredient, it is shown that the content of the metallic-oxide system compound in an ingredient is decreasing serially in the direction of a substrate from the front face.

[0018] The organic-inorganic compound inclination ingredient of this invention is characterized by containing the complex in which the metal system compound carried out the chemical bond to the organic high molecular compound, and the complex by such chemical bond can be made to form easily by the approach of this invention explained later.

[0019] Although the metal nitride system compound which especially a limit does not have about the class of metal system compound in the inclination ingredient of this invention, and comes to carry out a chemical bond to an organic high molecular compound through a metallic-oxide system compound or a metallic-oxide system compound can be mention, that in which it is form with a sol-gel method and deals is desirable, and can mention preferably the oxide system compound of the metal choose, for example from silicon, titanium, a zirconium, and aluminum as such a metal system compound. These metal system compounds may contain one sort of metals, and may contain two or more sorts of metals.

[0020] Moreover, as a content of the above-mentioned metal system compound in the inclination ingredient of this invention, although there is especially no limit, it is metallic-oxide conversion and is 5 - 98 % of the weight usually 50 - 90% of the weight of the range especially preferably 20 to 98% of the weight preferably. What is necessary is not to be restricted that what is necessary is [especially] just what can be film-production-ized as the polymerization degree and molecular weight of an organic high molecular compound, but just to select suitably according to the class of high molecular compound, desired paint film physical properties, etc. Furthermore, the thing of the range 5 micrometers or less of the thickness of whose are 0.01-1.0 micrometers is suitable for especially the inclination ingredient of this invention from points, such as lopsidedness and paint film engine performance.

[0021] Such an organic-inorganic compound inclination ingredient can be efficiently manufactured by the approach of this invention shown below. The metal content radical which can be first combined with a metallic oxide or a metal nitride polymer by hydrolysis in the (A) molecule in the approach of this invention (A hydrolysis nature metal content radical may be called hereafter.) The organic high molecular compound which it has, and metallic compounds which can form a metallic oxide by (B) (b) hydrolysis (hydrolysis nature metallic compounds may be called hereafter) Or ** it does not carry out hydrolysis processing of the mixture with a (b) metal nitride polymer, hydrolysis processing of is done, and coating liquid is prepared.

[0022] As a metal in the metallic compounds which can form a metallic oxide by hydrolysis which is the metal content radical and (B) (b) component which can be combined with a metallic oxide or a metal nitride polymer by hydrolysis in the organic high molecular compound which is the above-mentioned (A) component, or the metal nitride polymer of a (b) component, as being chosen, for example from silicon, titanium, a zirconium, and aluminum, one sort can be preferably mentioned as it is few.

[0023] The organic high molecular compound which has the metal content radical which can be combined with a metallic oxide or a metal nitride polymer by hydrolysis in the molecule which is the above-mentioned (A) component can obtain the monomer which has for example, this metal content radical, and the monomer which does not contain a metal copolymerization or by carrying out condensation polymerization.

[0024] As a metal content radical which can be combined with a metallic oxide or a metal nitride polymer by hydrolysis here, it is a general formula (I), for example.

- M1R1n-1 - (I)

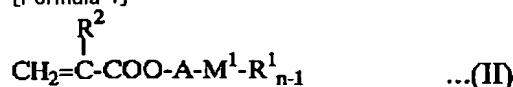
(Although R1 is a hydrolysis nature machine or an un-hydrolyzing nature machine among a formula) By hydrolysis, when it is required to be the hydrolysis nature machine which can carry out a chemical bond to the (B) component and R1 is plurality, at least one of them every - R1 may be mutually the same and you may differ, and M1 is metal atoms, such as silicon, titanium, a zirconium, and aluminum, and n is the valence of the metal atom M1. The radical expressed can be mentioned.

[0025] In the above-mentioned general formula (I), as a hydrolysis nature machine which can carry out a chemical bond to the (B) component by hydrolysis of R1, halogen atoms, such as an alkoxyl group, an isocyanate radical, and a chlorine atom, an oxy-halogen radical, an acetylacetonate radical, etc. are mentioned, for example, and, on the other hand, a low-grade alkyl group etc. is preferably mentioned, for example as an un-hydrolyzing nature machine which does not carry out a chemical bond to the (B) component.

[0026] As a metal content radical expressed with the above-mentioned general formula (I) For example, a trimethoxysilyl radical, a triethoxy silyl radical, a tree n-propoxy silyl radical, A triisopropoxy silyl radical, a tree n-butoxy silyl radical, a TORIISO butoxy silyl radical, A tree sec-butoxy silyl radical, a tree tert-butoxy silyl radical, A trichlorosilyl radical, a dimethyl methoxy silyl radical, a methyl dimethoxy silyl radical, A dimethyl chlorosilyl group, methylchlorosilyl group, a tri-isocyanate silyl radical, Trimethoxy titanium radicals, such as a MECHIRUJI isocyanato silyl radical, a TORIETOKISHI titanium radical, A tree n-propoxy titanium radical, a triisopropoxy titanium radical, A tree n-butoxy titanium radical, a TORIISO butoxy titanium radical, To a tree sec-butoxy titanium radical, a tree tert-butoxy titanium radical, a TORIKURORO titanium radical, and a pan A trimethoxy zirconium radical, a TORIETOKISHI zirconium radical, a tree n-propoxy zirconium radical, A triisopropoxy zirconium radical, a tree n-butoxyzirconium radical, To a TORIISO butoxyzirconium radical, a tree sec-butoxyzirconium radical, a tree tert-butoxyzirconium radical, a TORIKURORO zirconium radical, and a pan A dimethoxy aluminum radical, a diethoxy aluminum radical, a G n-propoxy aluminum radical, A JIISO propoxy aluminum radical, a G n-butoxy aluminum radical, a JIISO butoxy aluminum radical, a G sec-butoxy aluminum radical, a G tert-butoxy aluminum radical, a TORIKURORO aluminum radical, etc. are mentioned.

[0027] A desired high molecular compound is obtained by carrying out radical copolymerization of the monomer which has the monomer which has the metal content radical expressed with an ethylene nature partial saturation radical and said general formula (I) as an example of the above-mentioned copolymerization, and an ethylene nature partial saturation radical, and does not contain a metal. Specifically, it is a general formula (II).

[Formula 1]



(— the inside of a formula, and R2 — a hydrogen atom or a methyl group, and A — an alkylene group — the alkylene group of carbon numbers 1-4, and R1, M1 and n are preferably the same as the above.) — one or more sorts of acrylic ester which uses the alkyl group containing the metal content radical expressed as an ester component (meta), and general formula (III)

[Formula 2]



(— a hydrogen atom or a methyl group, and X of R3 are the organic radicals of monovalence among a formula.) — the monomer which has the ethylene nature partial saturation radical expressed — especially — desirable — general formula (III-a)

[Formula 3]



(— R4 is an alkyl group, a cycloalkyl radical, an aryl group, or an aralkyl radical among a formula, and R3 is the same as the above.) — the approach of carrying out radical copolymerization of one or more sorts of acrylic ester expressed (meta) can be mentioned.

[0028] The radical in which macromolecule quantification by condensation is possible instead of the above-mentioned ethylene nature partial saturation radical as an example of condensation polymerization on the other hand, For example, the monomer which has the metal content radical expressed with two or more the functional groups and said general formulas (I) which generates amide association, an ester bond, or a urethane bond by condensation, A desired high molecular compound is obtained by the approach of carrying out condensation polymerization of the monomer which has the radical in which macromolecule quantification by condensation is possible, for example, two or more functional groups which generate amide association, an ester bond, or a urethane bond by condensation, and does not contain a metal content radical etc.

[0029] Condensation polymerization of the amine component and acid component which have the metal content radical as which one of components is expressed in said general formula (I) is carried out, condensation polymerization of the approach of making a polyamide forming, the alcoholic component which has a certain metal content radical as which it is, and it crawls and one [a gap or] component is expressed in said general formula (I), and the acid component is carried out, and, specifically, the method of making polyester form etc. is mentioned.

[0030] the above-mentioned (B) (**) — as the metallic compounds (hydrolysis nature metallic compounds) which can form a metallic oxide by hydrolysis which is a component — a general formula (IV)

M2R5m — (IV)

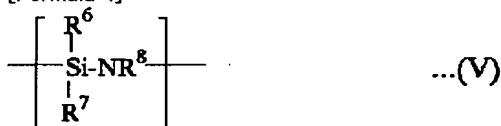
(Although R5 is a hydrolysis nature machine or an un-hydrolyzing nature machine among a formula) At least two are a hydrolysis nature machine. At least one [and] two or more R5 may be mutually the same, and you may differ, and it is the hydrolysis nature machine which can carry out a chemical bond to the (A) component by hydrolysis, and m is [M2 is metal atoms, such as silicon, titanium, a zirconium, and aluminum, and] the valence of the metal atom M2. The metallic compounds expressed can be mentioned.

[0031] As a hydrolysis nature machine of R5 in the above-mentioned general formula (IV), halogen atoms, such as an alkoxy group, an isocyanate radical, and a chlorine atom, an oxy-halogen radical, an acetylacetonate radical, etc. are mentioned, for example, and, on the other hand, a low-grade alkyl group, an aryl group, an alkenyl radical, etc. are preferably mentioned as an un-hydrolyzing nature machine, for example. What mixed the oligomer guided from the metallic compounds expressed with the above-mentioned general formula (IV) as these hydrolysis nature metallic compounds and two or more sorts of metallic compounds expressed with a general formula (IV) can be used.

[0032] As an example of metallic compounds expressed with the above-mentioned general formula (IV) A tetramethoxy silane, a tetra-ethoxy silane, tetra-n-propoxysilane, Tetra-isopropoxysilane, tetra-n-butoxysilane, tetrapod iso butoxysilane, Tetra-sec-butoxysilane, tetra-tert-butoxysilane, etc., The tetra-alkoxy titanium and the tetra-alkoxy zirconium corresponding to these to a list, further — trimethoxy aluminum and TORIE — an ibis — sial minium and tree n-propoxy aluminum — Triisopropoxy aluminum, tree n-butoxy aluminum, TORISO butoxy aluminum, tree sec-butoxy aluminum, A metal alkoxide or metal alkoxide oligomer, such as tree tert-butoxy aluminum, For example, the "methyl silicate 51" which is the alkoxysilane oligomer of a commercial item, Although a tetra-isocyanato silane, a methyl tri-isocyanate silane, tetra-chlorosilane, methyltrichlorosilane, etc. are mentioned further, "ethyl silicate 40" (all are the trade names by the COL coat company) etc. As this (B) (b) component, a metaled alkoxide is suitable. These may be used independently and may be used combining two or more sorts.

[0033] on the other hand — (B) (**) — as the metal nitride polymer which is a component — a general formula (V)

[Formula 4]



(— among a formula, although R6, R7, and R8 are the radical which carbon atoms, such as fluoro alkyl groups other than a hydrogen atom, an alkyl group, an alkenyl radical, an aryl group, aralkyl radicals, or these radicals, link with a silicon atom directly independently, respectively, an alkyl silyl radical, an alkylamino radical, or an alkoxy group, at least one of them is a hydrogen atom.) — the polysilazane of the number average molecular weight 100-50000 including the structural unit expressed etc. can be mentioned preferably.

[0034] It is under [polar-solvents / with alcohol, a ketone, the ether, etc. suitable when using a metal alkoxide as a (B) (b) component in the approach of this invention] setting. The high molecular compound of the aforementioned (A) component, and the mixture of the metal alkoxide of (B) (b) component When hydrolysis processing is carried out and 0-60 degrees C of solid acid are usually preferably used at the temperature of 20-40 degrees C using the cation exchange resin as acids, such as a hydrochloric acid, a sulfuric acid, and a nitric acid, or solid acid After removing it, it adjusts to the viscosity which was suitable for distilling off or adding and applying a solvent by request further, and coating liquid is prepared. When temperature is too low, hydrolysis does not progress, but when too high, hydrolysis progresses too much conversely, and there is a possibility that the lopsidedness of the inclination paint film obtained as a result may fall. in addition, (B) (**) — the polar-solvents solution containing the metal alkoxide of a component is prepared beforehand, an acid is added to this, the hydrolysis reaction is advanced, this thing and the (A) component may be mixed, and hydrolysis processing may be carried out further.

[0035] moreover, (B) (**) — as a component, when using isocyanate system metallic compounds and halogen system metallic compounds, or when using (B) (b) component, before membrane formation, hydrolysis processing is not performed but the approach of making it hydrolyze with the moisture in air is usually used in the time of membrane formation, or it or subsequent ones.

[0036] Since hydrolysis and a polycondensation may advance gradually depending on the class and after coating liquid preparation may change spreading conditions, when a mineral constituent adds dehydrating-agent, for example, sulfuric anhydride, serious NESHUUMU of an insoluble solid-state etc. to coating liquid, the fall of pot life can be prevented. In this case, after coating liquid removes this dehydrating agent, it is used for spreading.

[0037] Using the coating liquid obtained by doing in this way, on the substrate which consists of organic material next, as the thickness of a dry paint film, 5 micrometers or less of usual, and an interlayer application Preferably, 0.01-1.0 micrometers, so that it may become the range of 0.02-0.7 micrometers more preferably A dip coating method, a spin coat method, a spray coating method, the bar coat method, The organic - inorganic compound inclination ingredient of this invention is obtained by forming a paint film with well-known means, such as the knife coat method, the roll coat method, the blade coat method, the die coat method, and the gravure coat method, and carrying out stoving processing by well-known desiccation processing, for example, the temperature of about 40-150 degrees C.

[0038] this invention — setting — the (A) component and (B) (**) — by hydrolysis processing of mixture with the metal alkoxide of the components, while the hydrolysis nature metal content radical in the high molecular compound of the (A) component hydrolyzes, the metal alkoxide of (B) (b) component is also hydrolyzed and a polymerization is carried out a part. Next, while a substrate is adsorbed in the part of the flexible macromolecule chain in the high molecular compound of the (A) component by applying this coating liquid to the substrate (an organic base material being called) which consists of organic material, the hydrolysis part of the metal content radical of a side chain is located in the place distant from the substrate. While hydrolysis of the metal content radical of the above-mentioned side chain advances further by carrying out stoving processing of this paint film (B) Hydrolysis of the metal alkoxide of a (b) component and a polymerization also advance further, and the reactant radical generated by hydrolysis of the above-mentioned side chain at this time, for example, a silanol group, and (B) (**) — when hydrolysis of a component and a polymerization object carry out condensation (chemical bond), the complex the high molecular compound and the metallic-oxide system compound carried out [complex] the chemical bond forms.

[0039] moreover, the (A) component and (B) (**) — the isocyanate system of the components, halogen system metallic compounds, or (B) (**) — while a substrate is adsorbed in the part of the flexible macromolecule chain in the high molecular compound of the (A) component by applying the coating liquid which consists of mixture with a component to the substrate which consists of organic material, the hydrolysis nature metal content radical of a side chain is located in the place distant from the substrate. the reactant radical which generated this paint film by hydrolysis of the above-mentioned side chain while hydrolysis of the hydrolysis nature metal content radical of the above-mentioned side chain advanced with the moisture in air at the time of membrane formation or stoving processing, for example, a silanol group, and (B) (**) — the complex the metal nitride polymer of the hydrolyzate of the isocyanate system of a component or halogen system metallic compounds or (B) (b) component carried out [complex] the chemical bond forms. Therefore, the inclination complex with which the compound inclination ingredient of this invention is indicated by JP,8-283425,A differs fundamentally.

[0040] Thus, in the compound inclination ingredient of this invention formed on the organic base material, although the content of the metal system compound in an ingredient is about 100% on a front face, it decreases serially in the direction of a substrate, and becomes about 0% near the substrate. That is, the field which the compound inclination ingredient of this invention generally consisted of a filmy material formed on the organic base material, and is in contact with the organic base material of this filmy material on parenchyma is an organic macromolecule system compound component, and another open system side is a metal system compound.

[0041] In this invention, since a compound inclination ingredient is formed of said device, it is important after formation of a paint film time amount required to adsorb the substrate which consists of organic material in the part of a macromolecule chain, and to carry out grade maintenance of the liquid condition for several seconds at least generally. The solvent with which the fusibility solvent of an organic component and the fusibility solvent of a mineral constituent to be used usually differ from each other is used, and they need to have a miscibility. Moreover, in spreading in a coater or a spray method, also in order to make it adsorption of a high molecular compound take place before mineral constituents condense, in order for there to be no thickness spots and to acquire good inclination structure, it is desirable to make the vaporization point of the above-mentioned mineral constituent fusibility solvent higher than the vaporization point of an organic component fusibility solvent. In addition, an independent solvent is also usable if both organic component and mineral constituent can be dissolved.

[0042] There is especially no limit as a substrate which consists of organic material. For example, acrylic resin, such as polymethylmethacrylate, Olefin system resin, such as styrene resin, such as polystyrene and ABS plastics, polyethylene, and polypropylene, Polyester system resin, such as polyethylene terephthalate and polyethylenenaphthalate, Polyamide system resin, such as 6-nylon and 6 and 6-nylon, polyvinyl chloride system resin. The substrate which consists of cellulose system resin, such as polycarbonate system resin, polyphenylene sulfide system resin, polyphenylene ether system resin, polyimide system resin, and cellulose acetate, etc. can be mentioned.

[0043] In order that these substrates may raise adhesion with the inclination ingredient of this invention further, surface treatment can be performed by the oxidation style, an irregularity-ized method, etc. a request. As the above-mentioned oxidation style, corona discharge treatment, chromate treatment (wet), flame treatment, hot blast processing, ozone, UV irradiation processing, etc. are mentioned, for example, and the sandblasting method, a solvent approach, etc. are mentioned as an irregularity-ized method, for example. These surface treatment methods are suitably chosen according to the class of substrate.

[0044] In addition, the substrate which consists of organic material in this invention includes what has an organic system paint film on the front face of the base material which consists of the ingredient, for example, the metal system ingredient, glass and the ceramic system ingredient, the other various inorganic systems, or metal system ingredients other than an organic system ingredient.

[0045] Thus, the organic-inorganic compound inclination ingredient of obtained this invention while having said outstanding lopsidedness which was carried out, the property which eases the stress to the heat shrink of (1) substrate and the inorganic film or physical telescopic motion, and (2) refractive indexes with the mixing ratio of the (3) mineral constituents and the organic component which change continuously control of the surface structure at the time of membrane formation by the gestalt of arbitration and (4) mineral constituents which can control the lopsidedness simple is possible — etc. — it is useful for various applications as new high-performance material from having a property.

[0046] This invention also offers the coating agent which makes the coat which consists of this organic-inorganic compound inclination ingredient form on a base material again. As this coating agent, what consists of coating liquid which does not carry out hydrolysis processing of the organic high molecular compound which has the metal content radical which can be combined with a metallic oxide or a metal nitride polymer by hydrolysis, the metallic compounds which can form a metallic oxide by (B) (b) hydrolysis, or the mixture with a (b) metal nitride polymer, and which was obtained [the ** or] by carrying out hydrolysis processing can be preferably mentioned into the aforementioned (A) molecule.

[0047] This coating film can be used for the following application. First, it is used for the application as a paint film. This organic - inorganic compound inclination ingredient is excellent in the adhesive property over an organic base material, and a paint film front face can obtain the good rebound ace court film of adhesion while it is excellent in abrasion-proof nature, thermal resistance, etc. by preparing the coat layer which consists of this ingredient, for example on [various] plastic film from having the property of a metallic oxide or a metal nitride.

[0048] Next, it is used for the application as adhesives. Since a front face is a metal system compound while excelling in adhesion with an organic base material, as the inclination ingredient of this invention was described above, it excels in adhesion with inorganic or a metallic material. Therefore, it is suitable as adhesives with an organic material, inorganic, or a metallic material.

[0049] Furthermore, it is used for the application as an interlayer made to intervene between an organic base material and the coat layer which contains an inorganic system or a metal system ingredient at least. when you form the coat layer containing an inorganic system or a metal system ingredient on an organic base material, generally the adhesion of an organic base material and this coat layer should divide un-10 — it is, and is inferior to endurance and the problem of exfoliating by the passage of time or becoming easy to exfoliate with heat, moisture, etc. arises.

[0050] Since it has lopsidedness by making it intervene by making the inclination ingredient of this invention into an interlayer between the coat layers containing the above-mentioned organic base material, an inorganic system, or a metal system ingredient as this interlayer was described above, while excelling in adhesion with an organic base material Adhesion can be very good and the coat layer which is excellent also in adhesion with the coat layer containing the inorganic system or metal system ingredient prepared on it, consequently contains an inorganic system or a metal system ingredient on an organic base material can be made to form. In this invention, the range of 0.01-1.0 micrometers of thickness of this interlayer is 5 micrometers or less usually 0.02-0.7 micrometers more preferably.

[0051] Although there is especially no limit as a coat layer containing said inorganic system or a metal system ingredient and various coat layers can be formed, a rebound ace court layer, (4) inorganic system, a metal system material-for-optical-recording layer, an inorganic system, or a metal system dielectric layer etc. which contains (1) photocatalyst activity ingredient layer, (2) inorganic system or a metal system conductivity ingredient layer, (3) inorganic system, or a metal system ingredient, for example can be mentioned preferably.

[0052] Next, the coat layer containing each inorganic system or a metal system ingredient is explained.

(1) Photocatalyst activity ingredient layer : when the coat layer of photocatalyst activity ingredients, such as a titanium dioxide, is prepared in an organic base material front face, the problem that an organic base material deteriorates for a short time arises according to the photocatalyst operation. Therefore, to prepare the coat layer of photocatalyst activity ingredients, such as a titanium dioxide, on an organic base material according to a photocatalyst operation through the inorganic binder which cannot deteriorate easily is tried. However, an inorganic binder has the problem that adhesive strength with an organic base material is inadequate, and it is inferior to endurance.

[0053] When it is made to intervene between an organic base material and the coat layer of a photocatalyst activity ingredient by making the inclination ingredient of this invention into an interlayer, it excels in adhesion with an organic base material, and moreover, since a front face is a metal system compound mostly, a top with sufficient adhesion with the coat layer of a photocatalyst activity ingredient, an interlayer cannot deteriorate easily due to a photocatalyst operation, and it can fully protect an organic base material.

[0054] Moreover, the inclination ingredient of this invention can be made to be placed between front faces as an interlayer between the metal system base materials and photocatalyst activity ingredient layers which have an organic system paint film. Like the case of the above-mentioned organic base material, this interlayer is excellent in adhesion with an organic system paint film, and moreover, adhesion with the coat layer of a photocatalyst activity ingredient cannot deteriorate easily due to a photocatalyst operation a good top, and it can fully protect an organic system paint film. It is useful when preparing a photocatalyst activity ingredient layer especially as such an application on the steel plate for automobiles which has an organic system paint film on a front face.

[0055] As a metal system base material which has an organic system paint film on a front face, the thing in which the organic system paint film was formed can be mentioned, for example to metal system base materials, such as cold rolled sheet steel, a galvanized steel sheet, aluminum / zinc alloy plating steel plate, a stainless steel plate, an aluminum plate, and an aluminium alloy plate. It is especially effective when the coat layer of the photocatalyst activity ingredient prepared on it when using the inclination ingredient of this invention as such an interlayer is the high titanium dioxide of photocatalyst ability.

[0056] (2) — inorganic system or metal system conductivity ingredient layer: — the organic base material which has a conductive ingredient layer on a front face, especially plastic film are used for an electroluminescent element (EL element), a liquid crystal display component (LCD component), a solar battery, etc., and are further used as an electromagnetic wave electric shielding film, an antistatic nature film, etc. As a conductive ingredient used for such an application, inorganic systems, such as metallic oxides, such as indium oxide, tin oxide, a zinc oxide, cadmium oxide, and ITO (indiumtin oxide), and a metal like gold, platinum, silver, nickel, aluminum, and copper, or a metal system conductivity ingredient is used, for example. And these inorganic systems or a metal

system conductivity ingredient is usually formed as a thin film with a thickness of about 50-2000Å on organic base materials, such as plastic film, by well-known means, such as vacuum evaporation technique, the sputtering method, and the ion plating method. [0057] Thus, since the formed inorganic system or metal system conductivity ingredient layer has inadequate adhesion with an organic base material, it can raise adhesion with an organic base material, an inorganic system, or a metal system conductivity ingredient layer by making it intervene by making the inclination ingredient of this invention into an interlayer between an organic base material, this inorganic system, or a metal system conductivity ingredient layer. Moreover, when a transparent conductive film is required, transparency is hardly spoiled by making the interlayer which consists of an inclination ingredient of this invention intervene.

[0058] (3) — rebound ace court layer: containing an inorganic system or a metal system ingredient — surface hardness is good and the rebound ace court film which has the outstanding abrasion-proof nature and abrasion resistance is widely used as objects for surface pasting, such as windowpanes, such as a car and a building, and a plastics board for apertures, or objects for protection, such as a CRT display and a flat-panel display.

[0059] On the other hand, compared with a glass lens, a plastic lens is lightweight and is spreading quickly from excelling in safety, workability, fashionability, etc. in recent years. However, this plastic lens having the fault that a blemish tends to be attached compared with a glass lens, therefore covering that front face with a rebound ace court layer is performed.

[0060] The rebound ace court agent containing the inorganic system or metal system ingredients which consist of the metal and chelate compound which are chosen from the mixture of the mixture, the organotrialkoxysilane hydrolysis condensate, the alkoxysilane hydrolysis condensate, and colloidal silica which consist of an alkyl trihydroxy silane, and its partial condensate, colloidal silica and silicon denaturation acrylic resin, for example, a zirconium, aluminum, and titanium as an ingredient of the rebound ace court layer prepared in such a rebound ace court film and a plastic lens, and silicon denaturation acrylic resin, such as mixture, is used abundantly.

[0061] In order to form a rebound ace court layer on organic base materials, such as plastic film and a plastic lens, the approach of applying on an organic base material and carrying out desiccation processing of the rebound ace court agent containing an aforementioned inorganic system or an aforementioned metal system ingredient using a well-known approach, for example, the bar coat method, the knife coat method, the roll coat method, the blade coat method, the die coat method, the gravure coat method, a spray coating method, etc., so that desiccation thickness may be set to about 1-30 micrometers is usually used.

[0062] Thus, since the rebound ace court layer containing the formed inorganic system or metal system ingredient has inadequate adhesion with an organic base material, it can raise adhesion with the rebound ace court layer containing an organic base material, an inorganic system, or a metal system ingredient by making it intervene between an organic base material and this rebound ace court layer by making the inclination ingredient of this invention into an interlayer. Moreover, in a plastic lens, even if it makes the interlayer which consists of an inclination ingredient of this invention intervene, the fall of the transparency of this plastic lens, generating of an interference fringe, etc. are hardly brought about.

[0063] (4) — inorganic system, metal system material-for-optical-recording layer, inorganic system, or metal system dielectric layer: — in recent years as an optical recording medium which has the description of the rewriting possibility of, high density, mass storage capacity, the record reproducing head, non-contact, etc. The phase change disk using the phase change of amorphous ** was developed, and it has resulted [from the magneto-optic disk which records information using the flux reversal of a magnetic film using heat energy, such as semiconductor laser light, and is read using the magneto-optical effect, or the crystal] in utilization.

[0064] Generally such an optical recording medium has the structure where the laminating of a material-for-optical-recording layer, a dielectric layer, a metallic reflective layer, the organic protective layer, etc. was carried out one by one on the translucency resin substrate (organic base material), for example, substrates, such as polycarbonate and polymethylmethacrylate, and may prepare a dielectric substrate layer between a substrate and a material-for-optical-recording layer.

[0065] The phase change mold record ingredient of inorganic systems, such as the optical MAG mold record ingredient of inorganic systems, such as Tb-Fe, Tb-Fe-Co, Dy-Fe-Co, and Tb-Dy-Fe-Co, or TeOx, Te-germanium, Sn-Te-germanium, Bi-Te-germanium, Sb-Te-germanium, Pb-Sn-Te, and Tl-In-Se, is used for the material-for-optical-recording layer prepared on a substrate.

Moreover, inorganic system ingredients, such as SiN, SiO, SiO₂, and Ta₂O₅, are used for the dielectric substrate layer prepared between a substrate and a material-for-optical-recording layer by request. The material-for-optical-recording layer and dielectric substrate layer of said inorganic system are usually formed by well-known means, such as vacuum evaporation technique, the sputtering method, and the ion plating method.

[0066] Thus, since the formed inorganic system, the metal system material-for-optical-recording layer, or the inorganic system dielectric substrate layer has inadequate adhesion with a translucency resin substrate, it can raise adhesion with a substrate, a material-for-optical-recording layer, or a dielectric substrate layer by making it intervene by making the inclination ingredient of this invention into an interlayer between a translucency resin substrate, this material-for-optical-recording layer, or this dielectric substrate layer.

[0067] In addition, as a coat layer containing an inorganic system or a metal system ingredient, inorganic system infrared absorption agent layers, such as titanium oxide, a zinc oxide, indium oxide, tin oxide, zinc sulfide, antimony dope tin oxide (ATO), and tin dope indium oxide (ITO), the magnetic layer by which metal vacuum evaporation was carried out are mentioned.

[0068] This invention also offers the goods which have the coat layer which the charge of organic - inorganic binder which comes further to use the base material and this compound inclination ingredient which come to use the above-mentioned organic-inorganic compound inclination ingredient as adhesives, and this compound inclination ingredient are made to intervene as an interlayer, and contains an inorganic system or a metal system ingredient at least.

[0069] The metal system base material which the organic base material which has the coat layer which the organic-inorganic compound inclination ingredient of this invention is made to intervene as an interlayer, and contains an inorganic system or a metal system ingredient at least as an example of said base material, or the organic - inorganic compound inclination ingredient of this invention is made to intervene as an interlayer, and has a photocatalyst activity ingredient layer and with which the organic system paint film was prepared in the front face can be mentioned preferably.

[0070] Moreover, as an example of goods, the coat layer which contains an inorganic system or a metal system ingredient at least can mention preferably what is the rebound ace court layer containing (1) photocatalyst activity ingredient layer, (2) inorganic system or a metal system conductivity ingredient layer, (3) inorganic system, or a metal system ingredient and (4) inorganic system, a metal system material-for-optical-recording layer, an inorganic system, or a metal system dielectric layer.

[0071] As an application of the organic-inorganic compound inclination ingredient of this invention except for an above-mentioned

application — for example, (1) ferroelectric thin film (barium titanate —) The interlayer of UV cut film which consists of interlayer (2) metal vacuum evaporation thin films, such as lead titanate and strontium titanate, (3) The interlayer of the heat ray electric shielding film which consists of a metal vacuum evaporation thin film, the interlayer of the low reflection and the nonreflective coating film which consists of a (4) silica-titania cascade screen, (5) The interlayer of the HUD combiner film which consists of a silica-titania cascade screen, (6) Interlayer for thin films which made the inorganic oxide dope a functional molecule with a sol-gel method (in mineral constituents, such as a silica) A fluorochrome, the coloring matter for laser, a photochromic ingredient, electrochromic materials, The use as film for immobilization to which the chemical bond of the molecules, such as an enzyme, an antibody, and protein, is carried out by the coupling reaction using the under coat the thin film which distributed the nonlinear engineering ingredient, and for the inorganic system antibacterial material for (7) spreading, and the OH radical of the inclination film front face where (8) mineral constituents consist of a silica, [0072] The OH radical of the silica of an inclination film front face is used. (9) A silane system coupling agent and a titanate system coupling agent, The OH radical of the use as reaction sites, such as an aluminates system coupling agent and a zirconate system coupling agent, and the silica of (10) inclination film front face is used. the functional group in which a polymerization is possible is combined — making — the use as a graft reaction place, and **—proof coating (a titania —) of (11) plastics Multiple oxides, such as an alumina, a zirconia and a titania-silica, an alumina-silica, and a zirconia-silica, (12) Heat-resistant coating of plastics, bleed out prevention coating of (13) plastics front face (the bleed out to the front face of the additive in plastics is intercepted), (14) The antioxidizing film on the front face of plastics, the optical fiber which formed the cladding layer which used (15) transparency resin as the core layer by the inclination film, the rod lens which used transparency resin as the rod of a large diameter by (16) same as the above can be mentioned.

[0073]

[Example] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples.

[0074] It was made to react at 70 degrees C for 2.5 hours, after mixing formation methyl-methacrylate [product made from Wako Pure Chem Industry] 11.8g of example 1(1) organic-inorganic bipolar membrane, and 3-methacryloxy-propyl-trimethoxysilane [0.5by Shin-Etsu Chemical Co., Ltd.] g and agitating well, adding and agitating 2,2'-azobis isobutyronitrile [product made from Wako Pure Chem Industry] 0.2g to this. After reaction termination, after cooling to a room temperature, the polymerization object was dissolved into 246ml of acetones, 123ml of ethanol was added further, and the solution (a polymer solution is called hereafter.) of the organic high molecular compound of the (A) component was prepared.

[0075] On the other hand, it was dropped into tetra-ethoxy silane [product made from Wako Pure Chem Industry] 61.5ml, agitating a hydrochloric acid and 30.8ml of isopropanol solutions of 0.05g [/ml] hydrochloric-acid concentration, and churning was continued at the room temperature for 5 hours. After dropping this mineral constituent solution calmly into the polymer solution obtained above and agitating it at a room temperature for 4 hours, it diluted with 515ml of acetones, and after churning, it diluted with 738ml of ethanol further, and coating liquid was often prepared. Organic - inorganic bipolar membrane with a thickness of 0.6 micrometers was made to form by applying this coating liquid on a polymethylmethacrylate substrate with a spin coat method (for 1500rpm and 10 seconds), and carrying out stoving processing at 70 degrees C for 12 hours.

[0076] (2) evaluation (**) organic - inorganic bipolar membrane obtained by the lopsidedness above (1) — XPS equipment — using "PHI-5600 [the product made from ULVAC FAI]", argon sputtering (4kV) was performed at intervals of 5 minutes, the film was shaved, the content of the carbon atom on the front face of the film and a silicon atom was measured by X-ray photoelectron spectroscopy, and lopsidedness was investigated. A graph shows relation with the content of sputtering time amount (it is related to the membranous depth), a carbon atom, and a silicon atom to drawing 1 . This drawing shows having the outstanding lopsidedness.

[0077] (b) The titanium-dioxide coat film with a thickness of 0.4 micrometers was formed by making into an interlayer organic - inorganic bipolar membrane obtained by the endurance above (1) of a titanium-dioxide interlayer application, applying the photocatalyst coat agent which diluted "STS-01 [the Ishihara Sangyo Kaisha, Ltd. make]" with distilled water 3 times on this with a spin coat method (for 1500rpm and 10 seconds), and carrying out desiccation fixing at 70 degrees C for 12 hours. After putting this in in the sealing silica glass container and adjusting to the temperature of 60 degrees C, and 50% of relative humidity, the optical exposure (quantity of light 2.0 mW/cm2) was carried out using the black light, and aging of the permeability in the light (400-800nm) accompanying UV irradiation was measured. Aging of the permeability spectrum of this film in a light field is shown in drawing 12 .

[0078] Moreover, from aging of permeability with a wavelength [to UV irradiation time amount] of 500nm, the reduction rate of the permeability was evaluated and this was made into the characteristic of endurance evaluation. A graph shows the relation between UV irradiation days and the decrement of permeability with a wavelength of 500nm to drawing 13 . Drawing 12 and drawing 13 show having the outstanding endurance.

[0079] <Accelerated weathering test> Further, the accelerated weathering test was performed for this film using the sunshine weather meter (temperature of 60 degrees C inside the plane, 18 minutes in spray cycle 120 minutes), and change of light transmission and change of an appearance investigated the degree of degradation by the photocatalyst. Change of the visible-ray permeability to the exposure period of a sunshine weather meter is shown in drawing 14 . To 90% before a trial, for 20 days, the light transmission of 500nm is maintaining after progress mostly with 87%, and does not have an exterior change, and showed good weatherability.

[0080] Organic-inorganic bipolar membrane was made to form like an example 1 in example 2 example 1 except having used the polystyrene substrate instead of the polymethylmethacrylate substrate. About this film, lopsidedness was evaluated like the example 1. A graph shows relation with the content of sputtering time amount, a carbon atom, and a silicon atom to drawing 2 . This drawing shows having the outstanding lopsidedness.

[0081] Organic-inorganic bipolar membrane was made to form like an example 1 in example 3 example 1 except having used the polyethylene terephthalate film instead of the polymethylmethacrylate substrate. Lopsidedness was evaluated like the example 1 about this film. A graph shows relation with the content of sputtering time amount, a carbon atom, and a silicon atom to drawing 3 . This drawing shows having the outstanding lopsidedness.

[0082] Organic-inorganic bipolar membrane was made to form like an example 1 in example 4 example 1 except having used the polypropylene film instead of the polymethylmethacrylate substrate. Lopsidedness was evaluated like the example 1 about this film. A graph shows relation with the content of sputtering time amount, a carbon atom, and a silicon atom to drawing 4 . This drawing shows having the outstanding lopsidedness.

[0083] Organic - inorganic bipolar membrane was made to form like an example 1 in example 5 example 1 except having diluted and used coating liquid 5 times with ethanol / acetone partially aromatic solvent (capacity factors 1/1), and having adopted the dip

coating method (a part for 0.5cm/in pull-up rate) instead of the spin coat method. Lopsidedness was evaluated like the example 1 about this film. A graph shows relation with the content of sputtering time amount, a carbon atom, and a silicon atom to drawing 5. This drawing shows having the outstanding lopsidedness.

[0084] Organic-inorganic bipolar membrane was made to form like an example 1 instead of 61.5ml of tetra-ethoxy silanes in example 6 example 1 except having used tetraisopropoxy titanium [product made from Wako Pure Chem Industry] 84.0 ml. Lopsidedness was evaluated like the example 1 about this film. A graph shows relation with the content of sputtering time amount, a carbon atom, and a titanium atom to drawing 6. This drawing shows having the outstanding lopsidedness.

[0085] Organic-inorganic inclination bipolar membrane was made to form like an example 1 in example 7 example 1 except having used the polycarbonate substrate (the you pyrone made from Mitsubishi Engineering plastics, thickness of 400 micrometers) instead of the polymethylmethacrylate substrate. About this film, lopsidedness was evaluated like the example 1. A graph shows relation with the content of sputtering time amount, a carbon atom, and a silicon atom to drawing 15. This drawing shows having the outstanding lopsidedness.

[0086] An example 8 (1) Formation [of organic-inorganic bipolar membrane] [(A) In the preparation] 100 ml glass container of a component, methyl-methacrylate [product (it may be henceforth written as MMA) made from Wako Pure Chem Industry] 10.92g, and 3-methacryloxy-propyl-trimethoxysilane [Shin-Etsu Chemical Make (it may be henceforth written as MPTMS)] After having put in 2.71g, mixing and agitating well, 2,2'-azobis isobutyronitrile [product made from Wako Pure Chem Industry] 0.2g was added to this, and it sealed by covering to it. The radical polymerization reaction was performed at 70 degrees C for 2.5 hours, having placed this container all over the water bath, and agitating with a magnetic stirrer. After reaction termination, after cooling a polymerization object to a room temperature, 1.0g of polymerization objects was dissolved into 100ml of acetones, and the solution (a polymer solution is called hereafter) of the organic high molecular compound of the (A) component was prepared.

[0087] [(B) preparation of a component] — on the other hand — tetra — it was dropped gradually, agitating the solution which turns into a solution which dissolved ethoxy silane [special grade chemical made from Wako Pure Chem Industry (it may be henceforth written as TEOS)] 12g into 10ml of ethanol from 3.1g of concentrated hydrochloric acid, and 5ml of ethanol. This mixed solution was agitated at the room temperature for 5 hours, and it considered as the mineral constituent solution of the (B) component.

[0088] 10ml of [preparation of inclination film coating liquid] polymer solutions was diluted with 40ml of acetones, 40ml of ethanol was often added after churning, 10ml of mineral constituent solutions was added and agitated further, and inclination film coating liquid was prepared.

[0089] On the rotation cup of a [spin coat of inclination film] spin coater, the polyethylene terephthalate (PET) film [the lumiler T-60 by Toray Industries, Inc. and the film thickness of 188 micrometers] of 12cm angle was fixed, the above-mentioned inclination film coating liquid was carried on the film so that the front face of a film might be wet, the rotation cup was rotated in 1500rpm and 10 seconds after [of since it finishes wetting the whole film] 5 seconds, and the spin coat of the coating liquid was carried out. Organic-inorganic bipolar membrane with a thickness of 0.2 micrometers was made to form on a PET film by carrying out stoving processing of the applied film at 70 degrees C among oven for 12 hours.

[0090] (2) After being immersed in 0.05-N aqueous ammonia for 5 minutes, stoving of the ammoniation above-mentioned film was carried out at 70 degrees C among oven for 12 hours.

[0091] (3) Evaluation [spreading which is a photocatalyst titanium oxide coat agent] The titanium oxide coat film with a thickness of 0.15 micrometers was formed by applying the liquid which diluted the titanium oxide photocatalyst coat agent (Bisto RETA NDC[by Nippon Soda Co., Ltd.]-200C) with isopropanol 10 times with a spin coat method (for 1500rpm and 20 seconds) on this organic-inorganic bipolar membrane, and performing desiccation and heat treatment at 80 degrees C among oven for 12 hours.

[0092] About the film with which coating of the [accelerated weathering test] above-mentioned photocatalyst titanium oxide was carried out, the accelerated weathering test was performed using the sunshine weather meter (temperature of 60 degrees C inside the plane, 18 minutes in spray cycle 120 minutes), and change of light transmission and change of an appearance investigated the degree of degradation by the photocatalyst. Change of the visible-ray permeability to the exposure period of a sunshine weather meter is shown in drawing 16. To 81% before a trial, for 20 days, the light transmission of 500nm is maintaining after progress mostly with 79%, and does not have an exterior change, and showed good weatherability.

[0093] Moreover, when the photocatalyst titanium oxide coat agent was applied like the above about what heat-treated in the autoclave the film coated above (1) on condition that 130 degrees C and 1.7 kgf/cm² for 3 hours and the exposure trial by the sunshine weather meter was performed, the good result was obtained like the ammoniation film.

[0094] In the example 9 [corona discharge treatment of inclination interlayer] example 8, after coating inclination film coating liquid on a PET film [the lumiler T-60 by Toray Industries, Inc., and the film thickness of 188 micrometers], the film with which the coat of the photocatalyst titanium oxide was carried out like the example 8 was obtained except having processed for 3 seconds with the corona discharge processor (Kasuga Electric Works, Ltd. make, applied-voltage 150V, and current 15A). The accelerated weathering test according this film to a sunshine weather meter was performed. Change of the visible-ray permeability to the exposure period of a sunshine weather meter is shown in drawing 17. To 81% before a trial, for 20 days, the light transmission of 500nm is maintaining after progress mostly with 79%, and does not have an exterior change, and showed good weatherability.

[0095] In example 10 example 8, the 10g [/l.] acetone solution of the (A) component was prepared, having used the mole ratio of MMA/MPTMS as 10/1. On the other hand, the TEOS12g and 2.5g [of concentrated hydrochloric acid], and ethanol 5g mixed solution was dropped, and it agitated for 10 hours, and considered as mineral constituent liquid. (A) 3ml and 22ml of acetones of component liquid, and 4ml of mineral constituent liquid were mixed, further, it was easy to add 21ml of n-hexanols, and they were agitated. The PET film was immersed in this liquid, and it pulled up the rate for 15cm/, and coated. The lopsidedness of this coating film was measured like the example 1. The relation between sputtering time amount and the content of a silicon atom is shown in drawing 18. It turns out that it has the lopsidedness which was excellent from this drawing.

[0096] In example 11 example 8, the acetone solution whose (A) component is 10g/l. considering the mole ratio of MMA/MPTMS as 1/1, and 20/1, 100/1 was prepared. On the other hand, the TEOS12g and 2.5g [of concentrated hydrochloric acid], and ethanol 5g mixed solution was dropped, and it agitated for 10 hours, and considered as mineral constituent liquid. (A) 3ml and 22ml of acetones of component liquid, and 4ml of mineral constituent liquid were mixed, further, it was easy to add 21ml of n-hexanols, and they were agitated. The PET film was immersed in this liquid, and it pulled up the rate for 5.0cm/, and coated. The lopsidedness of this coating film was measured like the example 1. drawing 19 — the three above-mentioned kinds of MMA/MPTMS (mole ratio) — it attaches and the relation between sputtering time amount and the content of a silicon atom is shown. Change of the mole ratio of MMA/MPTMS shows that the inclination of an inclination is controllable from this drawing.

[0097] In example 12 example 8, the acetone solution whose (A) component is 10g/l. was prepared, having used the mole ratio of MMA/MPTMS as 10/1. On the other hand, the TEOS12g and 2.5g [of concentrated hydrochloric acid], and ethanol 5g mixed solution was dropped, and it agitated for 10 hours, and considered as mineral constituent liquid. (A) The coating liquid arbitrary dose **** and whose mineral constituent concentration are 1, 2, and 4 or 6 % of the weight about mineral constituent liquid was prepared to 1ml and 4ml of acetones of component liquid. The spin coat of this liquid was carried out on the PET film by the same approach as an example 8, and the organic-inorganic compound inclination film was obtained. The lopsidedness of this inclination film was measured like the example 1. The relation between the sputtering time amount in the inclination film of the four above-mentioned kinds of mineral constituent concentration and the content of a silicon atom is shown in drawing 20 . Change of mineral constituent concentration shows that the inclination of an inclination is controllable from this drawing.

[0098] Inclination film coating liquid was coated with the same approach as example 13 example 4 on the automobile steel plate (an acrylic / melanin resin coat) with which the black coating of 3cm angle was applied, and 70 degrees C dried among oven by it for 12 hours. the titanium oxide photocatalyst coat agent (NDC[by Nippon Soda Co., Ltd.]-200C) after processing the obtained automobile steel plate with the film for 3 seconds with plasma jet (PJ[by Kasuga Electric Works, Ltd.]- 1) — what diluted 1g by 0.08g of concentrated hydrochloric acid and 2-propanol 9g was applied with the spin coat method (for 1500rpm and 20 seconds), and the titanium oxide coat film with a thickness of 0.2 micrometers was formed by performing desiccation and heat treatment for 1 hour in [of 80 degrees C] oven. The sunshine weather meter (temperature in a testing machine of 60 degrees C, 18 minutes in spray cycle 120 minutes) performed the accelerated weathering test for the automobile steel plate with which coating of the above-mentioned photocatalyst was carried out, and change of the contact angle of water and an appearance was investigated. When the water contact angle was measured after progress for 20 days, it is less than 3 degrees of contact angles, and was changeless to a surface super-hydrophilic property compared with trial before. Moreover, neither an interference fringe nor milkiness was also seen, but good endurance was shown. The relation between the contact angle of an exposure period and the inclination film and an appearance is shown in Table 1.

[0099]

[Table 1]

表 1

		曝 露 時 間 (hr)					
		0	6 0	1 2 0	1 8 0	2 4 0	4 2 0
傾斜膜	接触角(度)	< 3	< 3	< 3	< 3	< 3	< 3
	外 観	良好	良好	良好	良好	良好	良好

[0100] The paint film was made to form like an example 1 in preparation of the polymer solution in example of comparison 1 example 1 except having changed the amount of a methyl methacrylate into 12g, without using 3-methacryloxy propyl trimethoxysilane. Lopsidedness was evaluated like the example 1 about this film. A graph shows relation with the content of sputtering time amount, a carbon atom, and a silicon atom to drawing 7 . As shown in this drawing, the film which has lopsidedness was not obtained.

[0101] The paint film was made to form like an example 1 in example of comparison 2 example 1 except having used the glass substrate instead of the polymethylmethacrylate substrate. Lopsidedness was evaluated like the example 1 about this film. A graph shows relation with the content of sputtering time amount, a carbon atom, and a silicon atom to drawing 8 . As shown in this drawing, the film which has lopsidedness was not obtained.

[0102] What added acrylic silicone resin solution "GS-1020" [Toagosei 6.5] g of example of comparison 3 marketing to toluene / 20g (capacity factors 1/1) of isopropanol partially aromatic solvents, and carried out churning mixing was applied with the spin coat method (for 1500rpm and 10 seconds) on the polymethylmethacrylate substrate, was dried at 70 degrees C for 12 hours, and the paint film as an interlayer was made to form. About the endurance of the titanium-dioxide interlayer application of this film, it evaluated like the example 1.

[0103] Aging of the permeability spectrum of this film in a light field is shown in drawing 9 , and a graph shows the relation between UV irradiation days and the decrement of permeability with a wavelength of 500nm to it at drawing 13 . This film did not show good endurance so that drawing 9 and drawing 13 might show.

[0104] What added inorganic adhesive "ethyl silicate 40" [COL Coat 8.1] g of example of comparison 4 marketing to toluene / 20g (capacity factors 1/1) of isopropanol partially aromatic solvents, and carried out churning mixing was applied with the spin coat method (for 1500rpm and 10 seconds) on the polymethylmethacrylate substrate, was dried at 70 degrees C for 12 hours, and the paint film as an interlayer was made to form. About the endurance of the titanium-dioxide interlayer application of this film, it evaluated like the example 1.

[0105] Aging of the permeability spectrum of this film in a light field is shown in drawing 10 , and a graph shows the relation between UV irradiation days and the decrement of permeability with a wavelength of 500nm to it at drawing 13 . This film did not show good endurance so that drawing 10 and drawing 13 might show.

[0106] Inorganic adhesive "ethyl silicate 40" [COL Coat 1.9] g of marketing was slowly dropped at what added acrylic silicone resin solution "GS-1020" [Toagosei 5.0] g of example of comparison 5 marketing to toluene / 10g (capacity factors 1/1) of isopropanol partially aromatic solvents, and carried out churning mixing, and churning mixing was carried out. Furthermore, toluene / 10g (capacity factors 1/1) of isopropanol partially aromatic solvents were added, churning mixing was carried out, and coating liquid was prepared. This coating liquid was applied with the spin coat method (for 1500rpm and 10 seconds) on the polymethylmethacrylate substrate, was dried at 70 degrees C for 12 hours, and the paint film as an interlayer was made to form. About the endurance of the titanium-dioxide interlayer application of this film, it evaluated like the example 1.

[0107] Aging of the permeability spectrum of this film in a light field is shown in drawing 11 , and a graph shows the relation between UV irradiation days and the decrement of permeability with a wavelength of 500nm to it at drawing 13 . Although film [this] showed good endurance somewhat, reduction in permeability was too checked, so that drawing 11 and drawing 13 might show.

[0108] In example of comparison 6 example 8, MPTMS was not used but the coating liquid for organic-inorganic bipolar membrane in which the (A) component and the (B) component have not carried out a chemical bond was compounded. Namely, methyl-

methacrylate [product made from Wako Pure Chem Industry] 12g and 2,2'-azobis isobutyronitrile [product made from Wako Pure Chem Industry] 0.2g were added in the 50ml glass container, and it sealed by covering. The radical polymerization reaction was performed at 75 degrees C for 2.5 hours, having placed this container all over the water bath, and agitating with a magnetic stirrer. After reaction termination, after cooling a polymerization object to a room temperature, the 0.2g of the above-mentioned polymerization objects was dissolved into 20ml of acetones, and the polymer solution which does not contain MPTMS was prepared.

[0109] On the other hand, the mineral constituent solution of the (B) component was obtained like the example 8 using the tetra-ethoxy silane. Henceforth, coating liquid is prepared like an example 8, a PET film is coated, and the result of the accelerated weathering test by the sunshine weather meter of the film which applied the photocatalyst titanium oxide coat agent further, and was obtained is shown in drawing 21. As for the light transmission in 500nm, it turned out for 83% before a trial to five days that are after progress, light transmission already fell to 45%, milkiness arose also in the exterior, and the film has deteriorated.

[0110] In example of comparison 7 example 1, the film to which the coat of the photocatalyst titanium oxide was carried out by the same approach as an example 1 was obtained instead of organic-inorganic bipolar membrane coating liquid except having applied the commercial under coat agent for photocatalyst titanium oxide coat agents (Bisto RETA NDC [by Nippon Soda Co., Ltd.] -100A) to the acrylic substrate. The accelerated weathering test according this film to a sunshine weather meter was performed. Change of the visible-ray permeability to the exposure period of a sunshine weather meter is shown in drawing 22. As for the light transmission in 500nm, it turned out for 76% before a trial to five days that are after progress, light transmission already fell to 57%, milkiness arose also in the exterior, and the film has deteriorated.

[0111] In example of comparison 8 example 8, the film to which the coat of the photocatalyst titanium oxide was carried out by the same approach as an example 8 was obtained except having used the commercial under coat agent for photocatalyst titanium oxide coat agents instead of organic-inorganic bipolar membrane coating liquid. The accelerated weathering test according this film to a sunshine weather meter was performed. Change of the visible-ray permeability to the exposure period of a sunshine weather meter is shown in drawing 23. As for the light transmission in 500nm, it turned out for 74% before a trial to 20 days that are after progress, light transmission fell to 66%, milkiness arose also in the exterior, and the film has deteriorated.

[0112] It was made to react at 70 degrees C for 2.5 hours, after mixing example 14 [(A) Preparation of component] methyl methacrylate 21.8g, and 3-methacryloxy-propyl-trimethoxysilane 5.41g and agitating well, adding and agitating 2,2'-azobis isobutyronitrile 0.4g to this. 4g of the obtained polymerization object was dissolved in the 2l. methyl ethyl ketone after radiational cooling, and the polymer solution of the (A) component was prepared.

[0113] It was slowly dropped into [(B) Preparation of component] one side, and a mixed solution (tetra-ethoxy silane 480g and ethanol 400g), agitating the mixed liquor of 40g of concentrated nitric acid, ethanol 200g, and 460g of water, churning was continued at the room temperature for 5 hours, and it considered as the mineral constituent solution of the (B) component.

[0114] [Preparation of inclination film coating liquid]

(A) 1.5l. of ethylcellosolve was added to the polymer solution of a component, after carrying out churning mixing, 500g of mineral constituent solutions of the (B) component was added to this, it agitated well, and inclination film coating liquid was prepared.

[0115] Coating was carried out to the PET film "lumiler T-60" (thickness of 50 micrometers, width of face of 330mm) by Toray Industries [, Inc.], Inc., and organic-inorganic bipolar membrane with a thickness of 0.1 micrometers was made to form by the KISUMA year bar method (0.1mm of wire sizes, line speed 10 m/min, drying temperature of 120 degrees C) by the "multi-coating machine M200" by [bar coat of inclination film] Hirano Tecseed. Lopsidedness was evaluated like the example 1 about this film. Relation with the content of sputtering time amount, a carbon atom, and a silicon atom is shown in a graph at drawing 24. It turns out that it has the lopsidedness which was excellent from this drawing.

[0116] 2g of the polymerization object obtained like example 15 example 14 was dissolved in 1l. methyl isobutyl ketone, and it considered as the polymer solution of the (A) component. 0.8l. of 1-butanol was added, after carrying out churning mixing, to this polymer solution, 200g of mineral constituent solutions of the (B) component in an example 14 was added, it agitated well to it, and inclination film coating liquid was prepared to it.

[0117] Coating of this was carried out to the acrylic board "a bitter taste rewrite" (thickness of 2mm, 300mmx300mm) by the Mitsubishi Rayon company with the Anest Iwata spray gun "W-88 series" in Ayr ** 0.2MPa, the spray distance of 15cm, and spray operating-speed 15 m/min, desiccation processing was carried out at 80 degrees C, and organic-inorganic ***** with a thickness of 0.15 micrometers was made to form. Lopsidedness was evaluated like the example 1 about this film. Relation with the content of sputtering time amount, a carbon atom, and a silicon atom is shown in a graph at drawing 25. It turns out that it has the lopsidedness which was excellent from this drawing.

[0118] the inside of the polymerization object obtained like example 16 example 14, and 1g — the Matsumoto Chemical Industry Co., Ltd. make — tetra — isocyanato "ORUGACHIKKUSU-silane Si 400" 56g was dissolved in 1l. toluene, and inclination film coating liquid was prepared.

[0119] Coating of this was carried out to the acrylic board "a bitter taste rewrite" (thickness of 2mm, 300mmx300mm) by the Mitsubishi Rayon company with the Anest Iwata spray gun "W-88 series" in Ayr ** 0.2MPa, the spray distance of 15cm, and spray operating-speed 15 m/min, desiccation processing was carried out at 25 degrees C, and organic-inorganic ***** with a thickness of 0.12 micrometers was made to form. Lopsidedness was evaluated like the example 1 about this film. Relation with the content of sputtering time amount, a carbon atom, and a silicon atom is shown in a graph at drawing 26. It turns out that it has the lopsidedness which was excellent from this drawing.

[0120] the inside of the polymerization object obtained like example 17 example 14, and 1g — the TONEN CORP. make — polysilazane "L110 (20-% of the weight xylene solution)" 0.29 l. was dissolved in the 0.71l. xylene, and inclination film coating liquid was prepared.

[0121] Coating of this was carried out to the PET film "the east rel mirror T-60" in the spin coater (1500rpm, 15 seconds), desiccation processing was carried out by 95 degrees C and 80%RH at 80 degrees C for 3 hours for 1 hour, and organic-inorganic ***** with a thickness of 0.12 micrometers was made to form. Lopsidedness was evaluated like the example 1 about this film. Relation with the content of sputtering time amount, a carbon atom, and a silicon atom is shown in a graph at drawing 27. It turns out that it has the lopsidedness which was excellent from this drawing.

[0122] example 18 [(A) preparation of component] styrene (Wako Pure Chem industry) 11.86g, and 3-methacryloxy-propyl-trimethoxysilane 1.42g — glassware with a capacity of 50ml — putting in — 2,2'-azobis isobutyronitrile 0.2g — in addition, it agitated and was made to dissolve completely Next, with the water bath adjusted to 70 degrees C, this container was heated for 5 hours and the polymerization of the styrene was carried out. Moved 0.2mg of obtained polystyrene copolymers to another

glassware, it was made to dissolve in 200ml of tetrahydrofuran solvents, and the polymer solution of the (A) component was prepared.

[0123] 40ml of tetrahydrofurans and 40ml of ethanol were put into glassware with a [preparation of inclination film] capacity of 100ml, and, in addition, it prepared inclination film coating liquid the above-mentioned polymer solution and 10ml of mineral constituent solutions at a time obtained in the example 1 to this.

[0124] It applies on a PET substrate with a spin coat method, and it was made to dry and organic-inorganic bipolar membrane was made to form by the approach according to an example 1 using the [spin coat of inclination film] above-mentioned coating liquid. Lopsidedness was evaluated like the example 1 about this film. Relation with the content of sputtering time amount, a carbon atom, and a silicon atom is shown in a graph at drawing 28. It turns out that it has the lopsidedness which was excellent from this drawing.

[0125] Example 19 It was made to react at 75 degrees C for 3 hours, after being easy to mix and agitating formation methyl methacrylate 10.92g of conductive film (1) organic-inorganic bipolar membrane, and 3-methacryloxy-propyl-trimethoxysilane 2.71g, adding and agitating 2,2'-azobis isobutyronitrile 0.2g to this. 1.0g of the obtained polymerization object was dissolved in 100ml of acetones, and the solution (a polymer solution is called hereafter.) of the organic high molecular compound of the (A) component was prepared.

[0126] It was dropped gradually, agitating the solution which, on the other hand, turns into a solution which dissolved tetra-ethoxy silane 12g in 10ml of ethanol from 3.1g of concentrated hydrochloric acid, and 5ml of ethanol. This mixed solution was agitated at the room temperature for 5 hours, and the mineral constituent solution of the (B) component was obtained. 40ml of ethanol was added, and after mixing 10ml of polymer solutions to 40ml of acetones and agitating to homogeneity, further, 10ml of mineral constituents was added, and it agitated until it became homogeneity.

[0127] Organic - inorganic bipolar membrane was made to form on a substrate, when this coating liquid is applied with a spin coat method (1500rpm, 10 seconds) on the polyethylene terephthalate film whose thickness is 0.188mm and carries out stoving at 40 degrees C for 12 hours. By depth profile measurement of XPS (the product made from ULVAC FAI, PHI-5600) of this film, the content ratio of carbon and silicon was measured and lopsidedness was investigated. A graph shows relation with the content of sputtering time amount, a carbon atom, and a silicon atom to drawing 29. It turns out that it has the lopsidedness which was excellent from this drawing.

[0128] (2) On the film obtained by production (1) of a conductive film, using the oxide target which consists of 90 % of the weight of indium oxide, and 10 % of the weight of stannic oxides, the transparence electric conduction film with a thickness of 40nm was made to form with DC magnetron sputtering equipment (Shimadzu, HS-720), and the conductive film was produced under the mixed-gas (it is 99:1 at volume ratio) ambient atmosphere of an argon and oxygen. Sheet resistance, light transmission, the squares friction test, and the heat test were investigated according to the following approaches using the obtained conductive film as the property. The result was summarized in Table 2.

[0129] (b) The transparence electric conduction film sheet resistance (Ω/\square) formed in sheet resistance one side was measured using the resistivity meter.

(b) The light transmission spectrophotometer (Shimadzu, UV-2100) was and the light transmission (%) of 550nm was measured.

(c) The squares tape method was enforced according to the squares friction test JIS K5400. After making 100 mass attachment and the Nichiban Scotch tape (trademark) stick the squares of 1mm angle to the paint film side of each test piece by pressure in a rotary cutter, 180 friction tests were carried out at the rate of 800 mm/min. Adhesion was evaluated by counting the existence of exfoliation among 100 masses.

[0130] (d) The temperature was lowered after 2-hour maintenance at 70 degrees C in oven, having heat resistance test applied it to -30 degrees C for 2 hours, and after that, it held at -30 degrees C for 2 hours, and 5 cycle **** and a thermo-cycle trial were carried out for the process which carries out a temperature up over 2 hours to 70 degrees C again. Measurement and the squares friction test of sheet resistance performed evaluation by checking the adhesion (existence of exfoliation in 100 masses) of a paint film.

[0131] The conductive film was produced by the same approach as an example 19 to the polycarbonate film with the organic-inorganic compound inclination film obtained in the example 20 example 7. The property of this conductive film is shown in Table 2.

[0132] It was dropped gradually, agitating the solution which turns into a solution which dissolved example 21 tetra-ethoxy silane 8.33g and methyl trimetoxysilane 1.36g in 10ml of ethanol from 3.1g of concentrated hydrochloric acid, and 5ml of ethanol. This mixed solution was agitated at the room temperature for 5 hours, and the mineral constituent solution was obtained.

[0133] After mixing 10ml of (A) polymer solutions of an example 19 to 40ml of acetones and agitating to homogeneity, 40ml of ethanol was added, further, 10ml of mineral constituent solutions was added, and the conductive film was completely produced by this actuation with the example 19 except having agitated until it became homogeneity.

[0134] By depth profile measurement of XPS (the product made from ULVAC FAI, PHI-5600) of organic-inorganic bipolar membrane before coating drawing 30 with the ITO film, the content ratio of carbon and silicon was measured and the result of having investigated lopsidedness was indicated. The property of this conductive film is shown in Table 2.

[0135] In example of comparison 9 example 19, adding and agitating 2,2'-azobis isobutyronitrile 0.2g to methyl methacrylate 12g, it was made to react at 75 degrees C for 3 hours, and 1.0g of the obtained polymerization object was dissolved in 100ml of acetones, except having prepared the solution of a polymethylmethacrylate compound, this actuation was completely performed with the example 19, and the conductive film was produced.

[0136] By depth profile measurement of XPS (the product made from ULVAC FAI, PHI-5600) of organic-inorganic bipolar membrane before coating drawing 31 with the ITO film, the content ratio of carbon and silicon was measured and the result of having investigated lopsidedness was indicated. The property of this conductive film is shown in Table 2.

[0137] The conductive film was completely produced by this actuation with the example 19 except having diluted with 20ml of acetones, and 20ml of ethanol 10ml of solutions of the polymethylmethacrylate compound prepared in the example 9 of example of comparison 10 comparison, and having considered as coating liquid. The property of this conductive film is shown in Table 2.

[0138]

[Table 2]

表 2

	導電性フィルムの特性				
	シート抵抗 (Ω/\square)	光線 透過率 (%)	基盤目 剥離試験	耐 熱 性	
				シート抵抗 (Ω/\square)	基盤目 剥離試験
実施例 19	300	85	94/100	320	92/100
実施例 20	280	83	100/100	280	100/100
実施例 21	280	85	95/100	280	93/100
比較例 9	310	84	50/100	1300	40/100
比較例 10	300	85	100/100	1850	35/100

[0139] Although conductivity and adhesion hardly change the conductive film of an example using the compound inclination film of this invention as an interlayer after a heat test as shown in Table 2, as for the thing of the example of a comparison, conductivity and adhesion are falling greatly after a heat test.

[0140] Example 22 In the rebound ace court film example 8, except having replaced the base material film with the polycarbonate film, it is the same approach as an example 8, and the film with the organic-inorganic compound inclination film was obtained. To this, the silicon rebound ace court agent made from Japanese DAKUROSHAMU Lock [the sol guard NP730] was formed using the bar coating machine so that the thickness after desiccation might be set to 4 micrometers, hardening processing of 2 hours was performed at 80 degrees C after that, and the desired base material with the rebound ace court film was obtained. In addition, when the pencil degree of hardness was measured about the film in front of a rebound ace court, only the polycarbonate film was H with the film which prepared F and the compound inclination film. The following trials were carried out about this base material with the rebound ace court film. The result was summarized in Table 3.

[0141] (1) Adhesion JIS The squares tape method was enforced according to K5400. After making 100 mass attachment and the Nichiban Scotch tape stick the squares of 1mm angle to the paint film side of each test piece by pressure in a rotary cutter, 180 friction tests were carried out at the rate of 300 mm/min. Adhesion was evaluated by counting the existence of exfoliation among 100 masses.

[0142] (2) Film degree of hardness JIS According to K5400, the pencil hardness test was carried out with reed MITSU Seiki Co., Ltd. make and a pencil scrape test machine, and the existence of the blemish of a paint film estimated the film degree of hardness.

[0143] (3) The antifriction trial of a paint film was carried out with wear-resistant reed MITSU Seiki Co., Ltd. make and a taper type abrasion tester (test condition: 200 counts of wear, 500g of loads, wear ring CS-10F). Whenever [after a trial / cloudiness] (Hayes value: deltaH%) estimated abrasion resistance.

[0144] (4) The temperature was lowered after 2-hour maintenance at 70 degrees C in oven, having heat resistance test applied it to -30 degrees C for 2 hours, and after that, it held at -30 degrees C for 2 hours, and 5 cycle **** and a thermo-cycle trial were carried out for the process which carries out a temperature up over 2 hours to 70 degrees C again. Evaluation was performed by checking the adhesion (existence of exfoliation in 100 masses) of a paint film by the squares tape method.

[0145] The base material with the rebound ace court film was obtained by the completely same actuation as an example 22 except having changed into the film (example 23) which carried out the coat of the inclination film at the polyethylene terephthalate film with a thickness of 0.188mm which produced an example 23 and 24 substrates in the example 19 from the polycarbonate film with a thickness of 0.4mm, and the acrylic film (example 24) with a thickness of 0.2mm. The evaluation result of this base material with the film was summarized in Table 3. About the film of an example 24, the content ratio of carbon and silicon was measured to drawing 32, lopsidedness was investigated to it, and the result was indicated to it by depth profile measurement of XPS (the product made from ULVAC FAI, PHI-5600) of the film in front of hard coating.

[0146] In addition, the pencil degrees of hardness of the film which prepared the compound inclination film in a polyethylene terephthalate film and it were 3H and 4H, respectively, and the pencil degrees of hardness of the film which prepared the compound inclination film in an acrylic film and it were 4H and 5H, respectively.

[0147] After mixing 10ml of polymer solutions of the (A) component of an example 8 to 40ml of example 25 acetones and agitating to homogeneity, 30ml of ethanol was added, further, 20ml of mineral constituent solutions of the (B) component of an example 8 was added, and it agitated until it became homogeneity, and the substrate with the rebound ace court film was completely obtained by the same actuation as an example 8 except having replaced the film base material with the polycarbonate film further. The evaluation result of this base material with the film was summarized in Table 3. By depth profile measurement of XPS (the product made from ULVAC FAI, PHI-5600) of the film in front of a rebound ace court, the content ratio of carbon and silicon was measured to drawing 33, lopsidedness was investigated to it, and the result was indicated to it.

[0148] Adding and agitating 2,2'-azobis isobutyronitrile 0.2g to methyl methacrylate 12g in example of comparison 11 example 8, it was made to react at 75 degrees C for 3 hours, and except having dissolved 1.0g of the obtained polymerization object in 100ml of acetones, having prepared the solution of a polymethylmethacrylate compound, having considered as the polymer solution, and having used the film base material as the polycarbonate film, this actuation was completely performed with the example 8, and the base material with the rebound ace court film was produced. Table 3 was asked for the evaluation result of this base material with the film.

[0149] On the polycarbonate film with an example of comparison 12 thickness of 0.4mm, the silicon rebound ace court agent made from Japanese DAKUROSHAMU Lock [the sol guard NP730] was formed in the bar coating machine so that the thickness after desiccation might be set to 4 micrometers, on it, hardening processing of 2 hours was performed at 80 degrees C after that, and the desired base material with the rebound ace court film was obtained on it. The evaluation result of this base material with the film was summarized in Table 3.

[0150]

[Table 3]

表 3

	密着性	膜硬度	耐摩耗性 ($\Delta H\%$)	耐熱性
実施例 2 2	100/100	4 H	8	100/100
実施例 2 3	94/100	6 H	8	92/100
実施例 2 4	100/100	6 H	6	100/100
実施例 2 5	100/100	4 H	8	100/100
比較例 1 1	44/100	3 H	28	34/100
比較例 1 2	10/100	2 H	55	0/100

[0151] As shown in Table 3, when the inclination film is used as a primer of a rebound ace court layer (examples 22-25), since it has inclination structure, inclination covering it from a mineral constituent into the structure at an organic component including a mineral constituent and an organic component, it is extremely excellent in the adhesive property of an organic base material and the both sides of a silicon system rebound ace court layer, and may fully demonstrate the engine performance of a rebound ace court layer.

[0152] On the other hand, since the mineral constituent and the organic component have not carried out a chemical bond when the acrylic silicone which does not have a chemical bond is used as a primer layer of a rebound ace court layer between the methyl methacrylate polymer of the (A) component, and the mineral constituent of the (B) component (example 11 of a comparison), it does not become inclination structure, but the adhesion of the interface of a mineral constituent and an organic component is low, and inferior to the engine performance. Moreover, since the rebound ace court agent itself is the silicon system of an inorganic material when there is no primer (example 12 of a comparison), it is lacking in adhesion with an organic base material, and inferior to the engine performance.

[0153] Example 26 The polycarbonate film with the inclination film obtained in the optical-recording-medium example 7 was set in the sputtering system, the SiN layer with a thickness of 8 micrometers was formed as a dielectric substrate layer (under coat) on the inclination film, and the under coat formation resin substrate was obtained. The desired magneto-optic-recording medium was obtained by setting an under coat formation resin substrate in a sputtering system, forming a TbDyFeCo layer with a thickness of 10 micrometers as a magneto-optic-recording layer on an under coat, and forming a SiN layer with a thickness of 8 micrometers as a dielectric protective layer (topcoat) further. The following trials were carried out about this magneto-optic-recording medium. The result was summarized in Table 4.

[0154] (1) Adhesion JIS between an under coat and a base material film The squares tape method was enforced according to K5400. After making 100 mass attachment and the Nichiban Scotch tape stick the squares of 1mm angle to the paint film side of each test piece by pressure in a rotary cutter, 180 friction tests were carried out at the rate of 300 mm/min. Adhesion was evaluated by counting the existence of exfoliation among 100 masses. Moreover, the temperature was lowered after 2-hour maintenance at 70 degrees C in oven, having covered it over -30 degrees C for 2 hours, and after that, it held at -30 degrees C for 2 hours, and 5 cycle **** and a thermo-cycle trial were carried out for the process which carries out a temperature up over 2 hours to 70 degrees C again, and adhesion was measured similarly.

[0155] (2) Film degree of hardness JIS According to K5400, the pencil hardness test was carried out with reed MITSU Seiki Co., Ltd. make and a pencil scrape test machine, and the existence of the blemish of a paint film estimated the film degree of hardness.

[0156] After mixing 10ml of polymer solutions of the (A) component of an example 19 to 40ml of example 27 acetones and agitating to homogeneity, 30ml of ethanol was added, further, 20ml of mineral constituent solutions of the (B) component of an example 19 was added, and the magneto-optic-recording medium was completely obtained by the same actuation as an example 19 except the actuation agitated until it became homogeneity. The evaluation result of this base material with the film was summarized in Table 4.

[0157] It kept at 75 degrees C, mixing and agitating example of comparison 13 methyl methacrylate 12g, and azobisisobutyronitril 0.2g, and the magneto-optic-recording medium was obtained by the same actuation as an example 26 except having made it react for 3 hours and having obtained the organic macromolecule component. The property of this magneto-optic-recording medium is shown in Table 4.

[0158] The magneto-optic-recording medium was created by the example 26 and this technique, without forming organic-inorganic bipolar membrane in an example of comparison 14 polycarbonate substrate. The property of this magneto-optic-recording medium is shown in Table 4.

[0159]

[Table 4]

表 4

	アンダーコートと樹脂基板との密着性		膜 硬 度
	ヒートサイクル前	ヒートサイクル後	
実施例 2 6	100/100	95/100	H
実施例 2 7	100/100	94/100	H
比較例 1 3	81/100	65/100	H
比較例 1 4	0/100	0/100	F

[0160] In addition, the curvature of each substrate of Ushiro who held under the high-humidity/temperature of 70 degrees C and 90%RH for 40 hours was measured, and when it investigated whether there would be any trouble in the writing and readout of data, the problem did not have both examples 26 and 27 and the examples 13 and 14 of a comparison.

[0161]
 [Effect of the Invention] The organic-inorganic compound inclination ingredient of this invention is organic-inorganic composite material containing the chemical bond object of an organic high molecular compound and a metal system compound. It has the component inclination structure where the content of this metal system compound changes in the thickness direction of an ingredient continuously. As new high-performance material as various applications, especially a coating agent It is suitable for the interlayers made to intervene between the coat layers containing adhesives and an organic base material, an inorganic system, or a metal system ingredient with a paint film, an organic material, inorganic, or a metallic material.

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the application of a new organic-inorganic compound inclination ingredient, its manufacture approach, and this inclination ingredient. This invention is organic-inorganic composite material containing the chemical bond object of an organic high molecular compound and a metal system compound in more detail. It has the component inclination structure where the content of this metal system compound changes in the thickness direction of an ingredient continuously. An organic-inorganic compound inclination ingredient useful for various applications as high-performance material, the coating agent for coat formation which becomes the approach list which manufactures this thing efficiently from this inclination ingredient. For example, it is related with the base material and goods which used the coating agent and this inclination ingredient which are used as an object for interlayers made to intervene between adhesives with a paint film, an organic material, inorganic, or a metallic material and an organic base material, an inorganic system, or a metal system ingredient layer. It is.

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PRIOR ART

[Description of the Prior Art] It becomes difficult to make it satisfied with a single high molecular compound in recent years with diversification of the demand about the engine performance of organic polymeric materials and a function, and adding and compound-izing a dissimilar material with a property which is different in a high molecular compound is performed. For example, physical-properties reforming by distributing reinforcement in organic polymeric materials is performed widely, the inorganic filler of the shape of powder, such as organic [, such as a carbon fiber, a glass fiber, a metal fiber, ceramic fiber, and an aramid fiber,], an inorganic fibrous material or a calcium carbonate, a silica, and an alumina, etc. is added, and, specifically, distributing homogeneity is performed. Moreover, research which makes a new function discover is also briskly done by mixing a high molecular compound of a different kind, making it compatibility-ize through a compatibilizer by the case, and polymer-alloy-izing.

[0003] On the other hand, the metal-ceramic compound functionally gradient material for which the presentation of an ingredient is changed little by little and the functionally gradient material which is the composite material with which properties completely differ on a table and the reverse side attracts attention for example, which has the thermal resistance of the ceramics and metalead reinforcement is developed as an airframe ingredient of a supersonic transport etc. recently.

[0004] such a functionally gradient material is classified into an inorganic inclination ingredient, an organic inclination ingredient, and an organic-inorganic compound inclination ingredient — having — and Space and the aeronautical-navigation field, the automobile field, the electronics field, the medical field, the energy field, and use [in / a radiation, the shielding field of an electromagnetic wave, etc. / further] are expected, for example from mixing two or more ingredients, for example, two or more inorganic materials of a different kind, two or more organic materials of a different kind or one or more sorts of organic materials, and one or more sorts of inorganic materials, making the physical properties of two or more component ingredients discover by controlling the distribution density which changes with locations, orientation, etc., and getting.

[0005] by the way, the so-called Honda-Fujishima effectiveness ["an industrial-chemistry magazine" by which the photolysis of the water is carried out to hydrogen and oxygen by making semi-conductors, such as a titanium dioxide, into a photoelectrical pole — since the 72nd volume, and the 108th — 113-page (1969)] were found out, development and utilization research of a photocatalyst have come to be done briskly. If semi-conductor particles, such as a titanium dioxide, are excited with the light of the energy more than that band gap, an electron will arise in a conduction band, and an electron hole will be generated in a valence band, and this photocatalyst will be rich in this energy, and will use an electronic-electron hole pair.

[0006] Such a photocatalyst is applied, for example, deodorization, antifouling, antibacterial, sterilization, decomposition, removal of the various matter which poses a problem on the environmental pollution in waste water and waste gas further, etc. are considered. Although metallic sulfide, such as metallic oxides, such as the compound which has the semi-conductor-property of former versatility as a photocatalyst, for example, a titanium dioxide, an iron oxide, tungstic oxide, and a zinc oxide, a cadmium sulfide, and zinc sulfide, etc. is known, the titanium dioxide, especially the anatase mold titanium dioxide are useful as a practical photocatalyst in these. This titanium dioxide shows the photocatalyst activity which was excellent by absorbing the light of the specific wavelength of the ultraviolet-rays field included in everyday light, such as sunlight, and demonstrates functions, such as antifouling, deodorization, antibacterial, air cleaning, water purification, and a super-hydrophilic property, by the powerful oxidation originating in this photocatalyst operation.

[0007] Such a photocatalyst function that photocatalysts, such as a titanium dioxide, have is demonstrated effectively, and research which uses it industrially is done briskly now. For example, it will be possible to give the operation which disassembles the organic substance into an ingredient front face only by irradiating light, and it will be begun to put dirt in practical use with pile glass, a tile, a toilet bowl, etc., if a photocatalyst is covered on the surface of an ingredient or is made to mix into the paint film on the front face of an ingredient. Moreover, development research of the various functional products using this photocatalyst is performed positively. the building materials which disassemble the nitrogen oxides used as the ringleader of (1) air pollution with solar light energy and (2) — while carrying out spontaneous decomposition of the adhering dirt which comes to cover a glass front face with a transparent photocatalyst [for example,] Utilization of the agent for waste water treatment which comes to cover titanium-dioxide impalpable powder to the window film stuck on side front faces, such as glass which has antibacterial effectiveness, and a glass window which comes to prepare a photocatalyst layer in a film front face using the super-hydrophilic property and antifouling property ability of (3) photocatalysts, and (4) silica-gel particle is considered.

[0008] However, photocatalysts, such as a titanium dioxide with a photocatalyst function, are not simply supported to organic substrates, such as plastics, but need a certain binder in many cases. Moreover, if this photocatalyst is directly coated on an organic substrate or is made to mix into this base material, the problem which says that it does not escape that an organic substrate deteriorates according to a photocatalyst operation for a short time will arise.

[0009] Although to prepare the coating film of photocatalysts, such as a titanium dioxide, through organic system adhesives etc. on an organic substrate in order to solve such a problem is also tried, the adhesive property of a binder and a photocatalyst object falls with time in this case, or the situation which is not desirable as for generating of nebula-izing and the interference color etc. is invited. Moreover, although to prepare the coating film of photocatalysts, such as a titanium dioxide, through inorganic system adhesives etc., for example on an organic substrate is also tried, in this case, an adhesive property with a substrate is not enough, or a crack etc. occurs in the glue line itself gradually, and the situation which is not desirable as for an adhesive fall with a binder and a base with time as a result, generating of nebula-izing and the interference color, etc. is invited. Moreover, to develop the microcapsule which covered photocatalysts, such as a titanium dioxide, with the silica, to mix this microcapsule into an organic base, and to give deodorization and an antibacterial function is tried. Since a photocatalyst cannot expose such a microcapsule to a

front face easily, many minute holes exist in the capsule and the small organic substance of a molecule can enter while degradation of an organic substrate is controlled, a catalyst function is demonstrated effectively. However, it is also difficult for the microcapsule of such structure to make the photocatalyst activity into high activity, and it is difficult to fully apply the hydrophilization phenomenon which is another description of a photocatalyst. Moreover, complicated actuation is needed for the manufacture approach, and it has the fault of not escaping a manufacturing cost costing dearly.

[0010] On the other hand, the layer which consists of various inorganic systems or metal system ingredients other than said photocatalyst activity ingredient, for example, a conductive ingredient, a rebound ace court agent, material for optical recording, magnetic powder, an infrared absorption ingredient, etc. is prepared on a plastics base material, and producing high-performance material is performed widely. Since adhesion with a base material is generally inadequate when preparing such an inorganic system or a metal system ingredient layer on a plastics base material, an inorganic system primer layer is prepared on a plastics base material, and the method of making an inorganic system or a metal system ingredient layer form on it is used well. However, in this approach, although the adhesion with an inorganic system primer layer, an inorganic system, or a metal system ingredient layer was good, the adhesion of a plastics base material and an inorganic system primer layer had the problem of it being inferior to heat-resistant adhesion, or adhesion falling by the passage of time rather than was necessarily enough. Therefore, development of the technique of making an inorganic system or a metal system ingredient layer forming with sufficient adhesion on a plastics base material was desired.

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EFFECT OF THE INVENTION

[Effect of the Invention] The organic - inorganic compound inclination ingredient of this invention is between the coat layers in which it is organic-inorganic composite material containing the chemical bond object of an organic high molecular compound and a metal system compound, and it has the component inclination structure of changing in the thickness direction of an ingredient continuously, and various applications are included as new high-performance material, and the content of this metal system compound includes adhesives and an organic base material, an inorganic system, or a metal system ingredient with a paint film, an organic material, inorganic, or a metallic material as a coating agent. It is suitable for the interlayers made to intervene.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention is the basis of such a situation. The new various applications as high-performance material, For example, it is prepared between a paint film, and an organic material, inorganic or adhesives with a metallic material, an organic base material and a photocatalyst paint film. For applications, such as an interlayer which prevents degradation of an organic base material, and an interlayer which raises adhesion with an organic base material, an inorganic system, or a metal system ingredient layer, [useful] A presentation aims at offering the method of manufacturing efficiently the organic-inorganic compound inclination ingredient which changes continuously, and this thing, and its application in the thickness direction.

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MEANS

[Means for Solving the Problem] The organic high molecular compound which has the metal content radical which can be combined with a metallic oxide or a metal nitride polymer by hydrolysis in a molecule as a result of repeating research wholeheartedly, in order that this invention persons may attain said purpose, and the metallic compounds which can form a metallic oxide by hydrolysis, Or the coating liquid which does not carry out hydrolysis processing of the mixture with a metal nitride polymer and which was obtained [the ** or] by carrying out hydrolysis processing is applied on an organic substrate. Organic-inorganic composite material containing the chemical bond object of the organic high molecular compound and metal system compound which are formed by carrying out stoving processing The content of the metal system compound in an ingredient is the new organic-inorganic compound inclination ingredient which has the component inclination structure of changing in the depth direction from the front face of an ingredient continuously, and it came to complete this invention for it being useful for said application based on a header and this knowledge.

[0013] Namely, this invention is organic-inorganic composite material containing the chemical bond object of (1) organic high molecular compound and a metal system compound. The organic-inorganic compound inclination ingredient with which content of the metal system compound in an ingredient is characterized by having the component inclination structure of changing in the depth direction from the front face of an ingredient continuously, (2) The coating agent characterized by making the coat which consists of the above-mentioned organic-inorganic compound inclination ingredient form on a base material, The coating agent used as an object for interlayer formation made to intervene preferably between the object for paint film formation and organic material to an organic base material, inorganic or the object for adhesives with a metallic material and an organic base material, and the coat layer that contains an inorganic system or a metal system ingredient at least, (3) The base material characterized by using the above-mentioned organic-inorganic compound inclination ingredient, (4) The charge of organic - inorganic binder characterized by using the above-mentioned organic-inorganic compound inclination ingredient as adhesives, And the goods characterized by having the coat layer which a (5) above-mentioned organic-inorganic compound inclination ingredient is made to intervene as an interlayer, and contains an inorganic system or a metal system ingredient at least are offered.

[0014] Moreover, the organic high molecular compound which has the metal content radical which can be combined with a metallic oxide or a metal nitride polymer by hydrolysis in the (A) molecule if said organic-inorganic compound inclination ingredient follows this invention and metallic compounds which can form a metallic oxide by (B) (b) hydrolysis, Or after [which does not carry out hydrolysis processing of the mixture with a (b) metal nitride polymer] carrying out [a ** or] hydrolysis processing and preparing coating liquid, the paint film which consists of the above-mentioned coating liquid can be formed on the substrate which consists of organic material, and it can manufacture by subsequently carrying out stoving processing.

[0015]

[Embodiment of the Invention] The organic - inorganic compound inclination ingredient of this invention has the component inclination structure of an organic high molecular compound and a metal system compound being organic-inorganic composite material containing the complex which comes to carry out a chemical bond, and organic - inorganic composite material which consists of this complex preferably, and changing continuously [the content of the metal system compound in an ingredient] from an ingredient front face to the depth direction.

[0016] The check of such component inclination structure can be performed by performing sputtering to the paint film front face of an organic-inorganic compound inclination ingredient prepared on the substrate which consists for example, of organic material, shaving the film on it, and measuring the content of the carbon atom on the front face of the film, and a metal atom by X-ray photoelectron spectroscopy etc. with time on it. If an example is given and explained concretely, drawing 1 will be set in the below-mentioned example 1. Organic - inorganic composite material with a thickness of 0.6 micrometers prepared on the polymethylmethacrylate substrate (as a metal atom) Although the paint film front face before performing sputtering is occupied by the silicon atom about about 100% as been the graph which shows relation with the content of the sputtering time amount in the paint film which becomes including a silicon atom, a carbon atom, and a silicon atom and shown in this drawing While the film follows on being deleted by sputtering and the content of the silicon atom on the front face of the film decreases, the content of a carbon atom increases and a film front face serves as only a carbon atom from the time of sputtering time amount passing over for about 30 minutes mostly.

[0017] That is, in this inclination ingredient, it is shown that the content of the metallic-oxide system compound in an ingredient is decreasing serially in the direction of a substrate from the front face.

[0018] The organic-inorganic compound inclination ingredient of this invention is characterized by containing the complex in which the metal system compound carried out the chemical bond to the organic high molecular compound, and the complex by such chemical bond can be made to form easily by the approach of this invention explained later.

[0019] Although the metal nitride system compound which especially a limit does not have about the class of metal system compound in the inclination ingredient of this invention, and comes to carry out a chemical bond to an organic high molecular compound through a metallic-oxide system compound or a metallic-oxide system compound can be mention, that in which it is form with a sol-gel method and deals is desirable, and can mention preferably the oxide system compound of the metal choose, for example from silicon, titanium, a zirconium, and aluminum as such a metal system compound. These metal system compounds may contain one sort of metals, and may contain two or more sorts of metals.

[0020] Moreover, as a content of the above-mentioned metal system compound in the inclination ingredient of this invention, although there is especially no limit, it is metallic-oxide conversion and is 5 - 98 % of the weight usually 50 - 90% of the weight of

the range especially preferably 20 to 98% of the weight preferably. What is necessary is not to be restricted that what is necessary is [especially] just what can be film-production-ized as the polymerization degree and molecular weight of an organic high molecular compound, but just to select suitably according to the class of high molecular compound, desired paint film physical properties, etc. Furthermore, the thing of the range 5 micrometers or less of the thickness of whose are 0.01-1.0 micrometers is suitable for especially the inclination ingredient of this invention from points, such as lopsidedness and paint film engine performance.

[0021] Such an organic-inorganic compound inclination ingredient can be efficiently manufactured by the approach of this invention shown below. The metal content radical which can be first combined with a metallic oxide or a metal nitride polymer by hydrolysis in the (A) molecule in the approach of this invention (A hydrolysis nature metal content radical may be called hereafter.) The organic high molecular compound which it has, and metallic compounds which can form a metallic oxide by (B) (b) hydrolysis (hydrolysis nature metallic compounds may be called hereafter) Or ** it does not carry out hydrolysis processing of the mixture with a (b) metal nitride polymer, hydrolysis processing of is done, and coating liquid is prepared.

[0022] As a metal in the metallic compounds which can form a metallic oxide by hydrolysis which is the metal content radical and (B) (b) component which can be combined with a metallic oxide or a metal nitride polymer by hydrolysis in the organic high molecular compound which is the above-mentioned (A) component, or the metal nitride polymer of a (b) component, as being chosen, for example from silicon, titanium, a zirconium, and aluminum, one sort can be preferably mentioned as it is few.

[0023] The organic high molecular compound which has the metal content radical which can be combined with a metallic oxide or a metal nitride polymer by hydrolysis in the molecule which is the above-mentioned (A) component can obtain the monomer which has for example, this metal content radical, and the monomer which does not contain a metal copolymerization or by carrying out condensation polymerization.

[0024] As a metal content radical which can be combined with a metallic oxide or a metal nitride polymer by hydrolysis here, it is a general formula (I), for example.

— M1R1_{n-1} — (I)

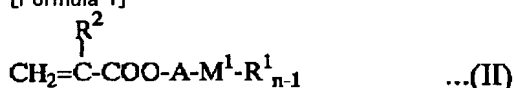
(Although R1 is a hydrolysis nature machine or an un-hydrolyzing nature machine among a formula) By hydrolysis, when it is required to be the hydrolysis nature machine which can carry out a chemical bond to the (B) component and R1 is plurality, at least one of them every — R1 may be mutually the same and you may differ, and M1 is metal atoms, such as silicon, titanium, a zirconium, and aluminum, and n is the valence of the metal atom M1. The radical expressed can be mentioned.

[0025] In the above-mentioned general formula (I), as a hydrolysis nature machine which can carry out a chemical bond to the (B) component by hydrolysis of R1, halogen atoms, such as an alkoxyl group, an isocyanate radical, and a chlorine atom, an oxy-halogen radical, an acetylacetonate radical, etc. are mentioned, for example, and, on the other hand, a low-grade alkyl group etc. is preferably mentioned, for example as an un-hydrolyzing nature machine which does not carry out a chemical bond to the (B) component.

[0026] As a metal content radical expressed with the above-mentioned general formula (I) For example, a trimethoxysilyl radical, a triethoxy silyl radical, a tree n-propoxy silyl radical, A triisopropoxy silyl radical, a tree n-butoxy silyl radical, a TORIISO butoxy silyl radical, A tree sec-butoxy silyl radical, a tree tert-butoxy silyl radical, A trichlorosilyl radical, a dimethyl methoxy silyl radical, a methyl dimethoxy silyl radical, A dimethyl chlorosilyl group, methylchlorosilyl group, a tri-isocyanate silyl radical, Trimethoxy titanium radicals, such as a MECHIRUJI isocyanato silyl radical, a TORIETOKISHI titanium radical, A tree n-propoxy titanium radical, a triisopropoxy titanium radical, A tree n-butoxy titanium radical, a TORIISO butoxy titanium radical, To a tree sec-butoxy titanium radical, a tree tert-butoxy titanium radical, a TORIKURORO titanium radical, and a pan A trimethoxy zirconium radical, a TORIETOKISHI zirconium radical, a tree n-propoxy zirconium radical, A triisopropoxy zirconium radical, a tree n-butoxyzirconium radical, To a TORIISO butoxyzirconium radical, a tree sec-butoxyzirconium radical, a tree tert-butoxyzirconium radical, a TORIKURORO zirconium radical, and a pan A dimethoxy aluminum radical, a diethoxy aluminum radical, a G n-propoxy aluminum radical, A JISO propoxy aluminum radical, a G n-butoxy aluminum radical, a JISO butoxy aluminum radical, a G sec-butoxy aluminum radical, a G tert-butoxy aluminum radical, a TORIKURORO aluminum radical, etc. are mentioned.

[0027] A desired high molecular compound is obtained by carrying out radical copolymerization of the monomer which has the monomer which has the metal content radical expressed with an ethylene nature partial saturation radical and said general formula (I) as an example of the above-mentioned copolymerization, and an ethylene nature partial saturation radical, and does not contain a metal. Specifically, it is a general formula (II).

[Formula 1]



(— the inside of a formula, and R2 — a hydrogen atom or a methyl group, and A — an alkylene group — the alkylene group of carbon numbers 1-4, and R1, M1 and n are preferably the same as the above.) — one or more sorts of acrylic ester which uses the alkyl group containing the metal content radical expressed as an ester component (meta), and general formula (III)

[Formula 2]



(— a hydrogen atom or a methyl group, and X of R3 are the organic radicals of monovalence among a formula.) — the monomer which has the ethylene nature partial saturation radical expressed — especially — desirable — general formula (III-a)

[Formula 3]



(— R4 is an alkyl group, a cycloalkyl radical, an aryl group, or an aralkyl radical among a formula, and R3 is the same as the above.) — the approach of carrying out radical copolymerization of one or more sorts of acrylic ester expressed (meta) can be mentioned.

[0028] The radical in which macromolecule quantification by condensation is possible instead of the above-mentioned ethylene nature partial saturation radical as an example of condensation polymerization on the other hand, For example, the monomer which has the metal content radical expressed with two or more the functional groups and said general formulas (I) which generates amide association, an ester bond, or a urethane bond by condensation, A desired high molecular compound is obtained by the approach of carrying out condensation polymerization of the monomer which has the radical in which macromolecule quantification by condensation is possible, for example, two or more functional groups which generate amide association, an ester bond, or a urethane bond by condensation, and does not contain a metal content radical etc.

[0029] Condensation polymerization of the amine component and acid component which have the metal content radical as which one of components is expressed in said general formula (I) is carried out, condensation polymerization of the approach of making a polyamide forming, the alcoholic component which has a certain metal content radical as which it is, and it crawls and one [a gap or] component is expressed in said general formula (I), and the acid component is carried out, and, specifically, the method of making polyester form etc. is mentioned.

[0030] the above-mentioned (B) (**) — as the metallic compounds (hydrolysis nature metallic compounds) which can form a metallic oxide by hydrolysis which is a component — a general formula (IV)

M2R5m — (IV)

(Although R5 is a hydrolysis nature machine or an un-hydrolyzing nature machine among a formula) At least two are a hydrolysis nature machine. At least one [and] two or more R5 may be mutually the same, and you may differ, and it is the hydrolysis nature machine which can carry out a chemical bond to the (A) component by hydrolysis, and m is [M2 is metal atoms, such as silicon, titanium, a zirconium, and aluminum, and] the valence of the metal atom M2. The metallic compounds expressed can be mentioned.

[0031] As a hydrolysis nature machine of R5 in the above-mentioned general formula (IV), halogen atoms, such as an alkoxyl group, an isocyanate radical, and a chlorine atom, an oxy-halogen radical, an acetylacetonate radical, etc. are mentioned, for example, and, on the other hand, a low-grade alkyl group, an aryl group, an alkenyl radical, etc. are preferably mentioned as an un-hydrolyzing nature machine, for example. What mixed the oligomer guided from the metallic compounds expressed with the above-mentioned general formula (IV) as these hydrolysis nature metallic compounds and two or more sorts of metallic compounds expressed with a general formula (IV) can be used.

[0032] As an example of metallic compounds expressed with the above-mentioned general formula (IV) A tetramethoxy silane, a tetra-ethoxy silane, tetra--n-propoxysilane, Tetra-isopropoxysilane, tetra--n-butoxysilane, tetrapod iso butoxysilane, Tetra--sec-butoxysilane, tetra--tert-butoxysilane, etc., The tetra-alkoxy titanium and the tetra-alkoxy zirconium corresponding to these to a list, further -- trimethoxy aluminum and TORIE -- an ibis -- sial minium and tree n-propoxy aluminum -- Triisopropoxy aluminum, tree n-butoxy aluminum, TORIISO butoxy aluminum, tree sec-butoxy aluminum, A metal alkoxide or metal alkoxide oligomer, such as tree tert-butoxy aluminum, For example, the "methyl silicate 51" which is the alkoxysilane oligomer of a commercial item, Although a tetra-isocyanato silane, a methyl tri-isocyanate silane, tetra-chlorosilane, methyltrichlorosilane, etc. are mentioned further, "ethyl silicate 40" (all are the trade names by the COL coat company) etc. As this (B) (b) component, a metalead alkoxide is suitable. These may be used independently and may be used combining two or more sorts.

[0033] on the other hand -- (B) (**) -- as the metal nitride polymer which is a component -- a general formula (V)

[Formula 4]



(-- among a formula, although R6, R7, and R8 are the radical which carbon atoms, such as fluoro alkyl groups other than a hydrogen atom, an alkyl group, an alkenyl radical, an aryl group, aralkyl radicals, or these radicals, link with a silicon atom directly independently, respectively, an alkyl silyl radical, an alkylamino radical, or an alkoxyl group, at least one of them is a hydrogen atom.)
 -- the polysilazane of the number average molecular weight 100-50000 including the structural unit expressed etc. can be mentioned preferably.

[0034] It is under [polar-solvents / with alcohol, a ketone, the ether, etc. suitable when using a metal alkoxide as a (B) (b) component in the approach of this invention] setting. The high molecular compound of the aforementioned (A) component, and the mixture of the metal alkoxide of (B) (b) component When hydrolysis processing is carried out and 0-60 degrees C of solid acid are usually preferably used at the temperature of 20-40 degrees C using the cation exchange resin as acids, such as a hydrochloric acid, a sulfuric acid, and a nitric acid, or solid acid After removing it, it adjusts to the viscosity which was suitable for distilling off or adding and applying a solvent by request further, and coating liquid is prepared. When temperature is too low, hydrolysis does not progress, but when too high, hydrolysis progresses too much conversely, and there is a possibility that the lopsidedness of the inclination paint film obtained as a result may fall. in addition, (B) (**) -- the polar-solvents solution containing the metal alkoxide of a component is prepared beforehand, an acid is added to this, the hydrolysis reaction is advanced, this thing and the (A) component may be mixed, and hydrolysis processing may be carried out further.

[0035] moreover, (B) (**) -- as a component, when using isocyanate system metallic compounds and halogen system metallic compounds, or when using (B) (b) component, before membrane formation, hydrolysis processing is not performed but the approach of making it hydrolyze with the moisture in air is usually used in the time of membrane formation, or it or subsequent ones.

[0036] Since hydrolysis and a polycondensation may advance gradually depending on the class and after coating liquid preparation may change spreading conditions, when a mineral constituent adds dehydrating-agent, for example, sulfuric anhydride, serious NESHUUMU of an insoluble solid-state etc. to coating liquid, the fall of pot life can be prevented. In this case, after coating liquid removes this dehydrating agent, it is used for spreading.

[0037] Using the coating liquid obtained by doing in this way, on the substrate which consists of organic material next, as the thickness of a dry paint film, 5 micrometers or less of usual, and an interlayer application Preferably, 0.01-1.0 micrometers, so that it may become the range of 0.02-0.7 micrometers more preferably A dip coating method, a spin coat method, a spray coating method, the bar coat method, The organic - inorganic compound inclination ingredient of this invention is obtained by forming a paint film with well-known means, such as the knife coat method, the roll coat method, the blade coat method, the die coat method, and the gravure coat method, and carrying out stoving processing by well-known desiccation processing, for example, the

temperature of about 40-150 degrees C.

[0038] this invention — setting — the (A) component and (B) (**) — by hydrolysis processing of mixture with the metal alkoxide of the components, while the hydrolysis nature metal content radical in the high molecular compound of the (A) component hydrolyzes, the metal alkoxide of (B) (b) component is also hydrolyzed and a polymerization is carried out a part. Next, while a substrate is adsorbed in the part of the flexible macromolecule chain in the high molecular compound of the (A) component by applying this coating liquid to the substrate (an organic base material being called) which consists of organic material, the hydrolysis part of the metal content radical of a side chain is located in the place distant from the substrate. While hydrolysis of the metal content radical of the above-mentioned side chain advances further by carrying out stoving processing of this paint film (B) Hydrolysis of the metal alkoxide of a (b) component and a polymerization also advance further. and the reactant radical generated by hydrolysis of the above-mentioned side chain at this time, for example, a silanol group, and (B) (**) — when hydrolysis of a component and a polymerization object carry out condensation (chemical bond), the complex the high molecular compound and the metallic-oxide system compound carried out [complex] the chemical bond forms.

[0039] moreover, the (A) component and (B) (**) — the isocyanate system of the components, halogen system metallic compounds, or (B) (**) — while a substrate is adsorbed in the part of the flexible macromolecule chain in the high molecular compound of the (A) component by applying the coating liquid which consists of mixture with a component to the substrate which consists of organic material, the hydrolysis nature metal content radical of a side chain is located in the place distant from the substrate. the reactant radical which generated this paint film by hydrolysis of the above-mentioned side chain while hydrolysis of the hydrolyzate nature metal content radical of the above-mentioned side chain advanced with the moisture in air at the time of membrane formation or stoving processing, for example, a silanol group, and (B) (**) — the complex the metal nitride polymer of the hydrolyzate of the isocyanate system of a component or halogen system metallic compounds or (B) (b) component carried out [complex] the chemical bond forms. Therefore, the inclination complex with which the compound inclination ingredient of this invention is indicated by JP.8-283425,A differs fundamentally.

[0040] Thus, in the compound inclination ingredient of this invention formed on the organic base material, although the content of the metal system compound in an ingredient is about 100% on a front face, it decreases serially in the direction of a substrate, and becomes about 0% near the substrate. That is, the field which the compound inclination ingredient of this invention generally consisted of a filmy material formed on the organic base material, and is in contact with the organic base material of this filmy material on parenchyma is an organic macromolecule system compound component, and another open system side is a metal system compound.

[0041] In this invention, since a compound inclination ingredient is formed of said device, it is important after formation of a paint film time amount required to adsorb the substrate which consists of organic material in the part of a macromolecule chain, and to carry out grade maintenance of the liquid condition for several seconds at least generally. The solvent with which the fusibility solvent of an organic component and the fusibility solvent of a mineral constituent to be used usually differ from each other is used, and they need to have a miscibility. Moreover, in spreading in a coater or a spray method, also in order to make it adsorption of a high molecular compound take place before mineral constituents condense, in order for there to be no thickness spots and to acquire good inclination structure, it is desirable to make the vaporization point of the above-mentioned mineral constituent fusibility solvent higher than the vaporization point of an organic component fusibility solvent. In addition, an independent solvent is also usable if both organic component and mineral constituent can be dissolved.

[0042] There is especially no limit as a substrate which consists of organic material. For example, acrylic resin, such as polymethylmethacrylate, Olefin system resin, such as styrene resin, such as polystyrene and ABS plastics, polyethylene, and polypropylene, Polyester system resin, such as polyethylene terephthalate and polyethylenenaphthalate, Polyamide system resin, such as 6-nylon and 6 and 6-nylon, polyvinyl chloride system resin, The substrate which consists of cellulose system resin, such as polycarbonate system resin, polyphenylene sulfide system resin, polyphenylene ether system resin, polyimide system resin, and cellulose acetate, etc. can be mentioned.

[0043] In order that these substrates may raise adhesion with the inclination ingredient of this invention further, surface treatment can be performed by the oxidation style, an irregularity-ized method, etc. a request. As the above-mentioned oxidation style, corona discharge treatment, chromate treatment (wet), flame treatment, hot blast processing, ozone, UV irradiation processing, etc. are mentioned, for example, and the sandblasting method, a solvent approach, etc. are mentioned as an irregularity-ized method, for example. These surface treatment methods are suitably chosen according to the class of substrate.

[0044] In addition, the substrate which consists of organic material in this invention includes what has an organic system paint film on the front face of the base material which consists of the ingredient, for example, the metal system ingredient, glass and the ceramic system ingredient, the other various inorganic systems, or metal system ingredients other than an organic system ingredient.

[0045] Thus, the organic-inorganic compound inclination ingredient of obtained this invention while having said outstanding lopsidedness which was carried out, the property which eases the stress to the heat shrink of (1) substrate and the inorganic film or physical telescopic motion, and (2) refractive indexes with the mixing ratio of the (3) mineral constituents and the organic component which change continuously control of the surface structure at the time of membrane formation by the gestalt of arbitration and (4) mineral constituents which can control the lopsidedness simple is possible — etc. — it is useful for various applications as new high-performance material from having a property.

[0046] This invention also offers the coating agent which makes the coat which consists of this organic-inorganic compound inclination ingredient form on a base material again. As this coating agent, what consists of coating liquid which does not carry out hydrolysis processing of the organic high molecular compound which has the metal content radical which can be combined with a metallic oxide or a metal nitride polymer by hydrolysis, the metallic compounds which can form a metallic oxide by (B) (b) hydrolysis, or the mixture with a (b) metal nitride polymer, and which was obtained [the ** or] by carrying out hydrolysis processing can be preferably mentioned into the aforementioned (A) molecule.

[0047] This coating film can be used for the following application. First, it is used for the application as a paint film. This organic - inorganic compound inclination ingredient is excellent in the adhesive property over an organic base material, and a paint film front face can obtain the good rebound ace court film of adhesion while it is excellent in abrasion-proof nature, thermal resistance, etc. by preparing the coat layer which consists of this ingredient, for example on [various] plastic film from having the property of a metallic oxide or a metal nitride.

[0048] Next, it is used for the application as adhesives. Since a front face is a metal system compound while excelling in adhesion with an organic base material, as the inclination ingredient of this invention was described above, it excels in adhesion with

inorganic or a metallic material. Therefore, it is suitable as adhesives with an organic material, inorganic, or a metallic material. [0049] Furthermore, it is used for the application as an interlayer made to intervene between an organic base material and the coat layer which contains an inorganic system or a metal system ingredient at least. When you form the coat layer containing an inorganic system or a metal system ingredient on an organic base material, generally the adhesion of an organic base material and this coat layer should divide un-10 — it is, and is inferior to endurance and the problem of exfoliating by the passage of time or becoming easy to exfoliate with heat, moisture, etc. arises.

[0050] Since it has lopsidedness by making it intervene by making the inclination ingredient of this invention into an interlayer between the coat layers containing the above-mentioned organic base material, an inorganic system, or a metal system ingredient as this interlayer was described above, while excelling in adhesion with an organic base material. Adhesion can be very good and the coat layer which is excellent also in adhesion with the coat layer containing the inorganic system or metal system ingredient prepared on it, consequently contains an inorganic system or a metal system ingredient on an organic base material can be made to form. In this invention, the range of 0.01–1.0 micrometers of thickness of this interlayer is 5 micrometers or less usually 0.02–0.7 micrometers more preferably.

[0051] Although there is especially no limit as a coat layer containing said inorganic system or a metal system ingredient and various coat layers can be formed, a rebound ace court layer, (4) inorganic system, a metal system material—for-optical-recording layer, an inorganic system, or a metal system dielectric layer etc. which contains (1) photocatalyst activity ingredient layer, (2) inorganic system or a metal system conductivity ingredient layer, (3) inorganic system, or a metal system ingredient, for example can be mentioned preferably.

[0052] Next, the coat layer containing each inorganic system or a metal system ingredient is explained.

(1) Photocatalyst activity ingredient layer : when the coat layer of photocatalyst activity ingredients, such as a titanium dioxide, is prepared in an organic base material front face, the problem that an organic base material deteriorates for a short time arises according to the photocatalyst operation. Therefore, to prepare the coat layer of photocatalyst activity ingredients, such as a titanium dioxide, on an organic base material according to a photocatalyst operation through the inorganic binder which cannot deteriorate easily is tried. However, an inorganic binder has the problem that adhesive strength with an organic base material is inadequate, and it is inferior to endurance.

[0053] When it is made to intervene between an organic base material and the coat layer of a photocatalyst activity ingredient by making the inclination ingredient of this invention into an interlayer, it excels in adhesion with an organic base material, and moreover, since a front face is a metal system compound mostly, a top with sufficient adhesion with the coat layer of a photocatalyst activity ingredient, an interlayer cannot deteriorate easily due to a photocatalyst operation, and it can fully protect an organic base material.

[0054] Moreover, the inclination ingredient of this invention can be made to be placed between front faces as an interlayer between the metal system base materials and photocatalyst activity ingredient layers which have an organic system paint film. Like the case of the above-mentioned organic base material, this interlayer is excellent in adhesion with an organic system paint film, and moreover, adhesion with the coat layer of a photocatalyst activity ingredient cannot deteriorate easily due to a photocatalyst operation a good top, and it can fully protect an organic system paint film. It is useful when preparing a photocatalyst activity ingredient layer especially as such an application on the steel plate for automobiles which has an organic system paint film on a front face.

[0055] As a metal system base material which has an organic system paint film on a front face, the thing in which the organic system paint film was formed can be mentioned, for example to metal system base materials, such as cold rolled sheet steel, a galvanized steel sheet, aluminum / zinc alloy plating steel plate, a stainless steel plate, an aluminum plate, and an aluminium alloy plate. It is especially effective when the coat layer of the photocatalyst activity ingredient prepared on it when using the inclination ingredient of this invention as such an interlayer is the high titanium dioxide of photocatalyst ability.

[0056] (2) — inorganic system or metal system conductivity ingredient layer: — the organic base material which has a conductive ingredient layer on a front face, especially plastic film are used for an electroluminescent element (EL element), a liquid crystal display component (LCD component), a solar battery, etc., and are further used as an electromagnetic wave electric shielding film, an antistatic nature film, etc. As a conductive ingredient used for such an application, inorganic systems, such as metallic oxides, such as indium oxide, tin oxide, a zinc oxide, cadmium oxide, and ITO (indiumtin oxide), and a metal like gold, platinum, silver, nickel, aluminum, and copper, or a metal system conductivity ingredient is used, for example. And these inorganic systems or a metal system conductivity ingredient is usually formed as a thin film with a thickness of about 50–2000Å on organic base materials, such as plastic film, by well-known means, such as vacuum evaporation technique, the sputtering method, and the ion plating method.

[0057] Thus, since the formed inorganic system or metal system conductivity ingredient layer has inadequate adhesion with an organic base material, it can raise adhesion with an organic base material, an inorganic system, or a metal system conductivity ingredient layer by making it intervene by making the inclination ingredient of this invention into an interlayer between an organic base material, this inorganic system, or a metal system conductivity ingredient layer. Moreover, when a transparent conductive film is required, transparency is hardly spoiled by making the interlayer which consists of an inclination ingredient of this invention intervene.

[0058] (3) — rebound ace court layer: containing an inorganic system or a metal system ingredient — surface hardness is good and the rebound ace court film which has the outstanding abrasion-proof nature and abrasion resistance is widely used as objects for surface pasting, such as windowpanes, such as a car and a building, and a plastics board for apertures, or objects for protection, such as a CRT display and a flat-panel display.

[0059] On the other hand, compared with a glass lens, a plastic lens is lightweight and is spreading quickly from excelling in safety, workability, fashionability, etc. in recent years. However, this plastic lens having the fault that a blemish tends to be attached compared with a glass lens, therefore covering that front face with a rebound ace court layer is performed.

[0060] The rebound ace court agent containing the inorganic system or metal system ingredients which consist of the metal and chelate compound which are chosen from the mixture of the mixture, the organotrialkoxysilane hydrolysis condensate, the alkoxysilane hydrolysis condensate, and colloidal silica which consist of an alkyl trihydroxy silane, and its partial condensate, colloidal silica and silicon denaturation acrylic resin, for example, a zirconium, aluminum, and titanium as an ingredient of the rebound ace court layer prepared in such a rebound ace court film and a plastic lens, and silicon denaturation acrylic resin, such as mixture, is used abundantly.

[0061] In order to form a rebound ace court layer on organic base materials, such as plastic film and a plastic lens, the approach of applying on an organic base material and carrying out desiccation processing of the rebound ace court agent containing an

forementioned inorganic system or an aforementioned metal system ingredient using a well-known approach, for example, the bar coat method, the knife coat method, the roll coat method, the blade coat method, the die coat method, the gravure coat method, a spray coating method, etc., so that desiccation thickness may be set to about 1–30 micrometers is usually used.

[0062] Thus, since the rebound ace court layer containing the formed inorganic system or metal system ingredient has inadequate adhesion with an organic base material, it can raise adhesion with the rebound ace court layer containing an organic base material, an inorganic system, or a metal system ingredient by making it intervene between an organic base material and this rebound ace court layer by making the inclination ingredient of this invention into an interlayer. Moreover, in a plastic lens, even if it makes the interlayer which consists of an inclination ingredient of this invention intervene, the fall of the transparency of this plastic lens, generating of an interference fringe, etc. are hardly brought about.

[0063] (4) — inorganic system, metal system material-for-optical-recording layer, inorganic system, or metal system dielectric layer: — in recent years as an optical recording medium which has the description of the rewriting possibility of, high density, mass storage capacity, the record reproducing head, non-contact, etc. The phase change disk using the phase change of amorphous ** was developed, and it has resulted [from the magneto-optic disk which records information using the flux reversal of a magnetic film using heat energy, such as semiconductor laser light, and is read using the magneto-optical effect, or the crystal] in utilization.

[0064] Generally such an optical recording medium has the structure where the laminating of a material-for-optical-recording layer, a dielectric layer, a metallic reflective layer, the organic protective layer, etc. was carried out one by one on the translucency resin substrate (organic base material), for example, substrates, such as a polycarbonate and polymethylmethacrylate, and may prepare a dielectric substrate layer between a substrate and a material-for-optical-recording layer.

[0065] The phase change mold record ingredient of inorganic systems, such as the optical MAG mold record ingredient of inorganic systems, such as Tb-Fe, Tb-Fe-Co, Dy-Fe-Co, and Tb-Dy-Fe-Co, or TeOx, Te-germanium, Sn-Te-germanium, Bi-Te-germanium, Sb-Te-germanium, Pb-Sn-Te, and Tl-In-Se, is used for the material-for-optical-recording layer prepared on a substrate.

Moreover, inorganic system ingredients, such as SiN, SiO, SiO₂, and Ta₂O₅, are used for the dielectric substrate layer prepared between a substrate and a material-for-optical-recording layer by request. The material-for-optical-recording layer and dielectric substrate layer of said inorganic system are usually formed by well-known means, such as vacuum evaporation technique, the sputtering method, and the ion plating method.

[0066] Thus, since the formed inorganic system, the metal system material-for-optical-recording layer, or the inorganic system dielectric substrate layer has inadequate adhesion with a translucency resin substrate, it can raise adhesion with a substrate, a material-for-optical-recording layer, or a dielectric substrate layer by making it intervene by making the inclination ingredient of this invention into an interlayer between a translucency resin substrate, this material-for-optical-recording layer, or this dielectric substrate layer.

[0067] In addition, as a coat layer containing an inorganic system or a metal system ingredient, inorganic system infrared absorption agent layers, such as titanium oxide, a zinc oxide, indium oxide, tin oxide, zinc sulfide, antimony dope tin oxide (ATO), and tin dope indium oxide (ITO), the magnetic layer by which metal vacuum evaporation was carried out are mentioned.

[0068] This invention also offers the goods which have the coat layer which the charge of organic – inorganic binder which comes further to use the base material and this compound inclination ingredient which come to use the above-mentioned organic–inorganic compound inclination ingredient as adhesives, and this compound inclination ingredient are made to intervene as an interlayer, and contains an inorganic system or a metal system ingredient at least.

[0069] The metal system base material which the organic base material which has the coat layer which the organic–inorganic compound inclination ingredient of this invention is made to intervene as an interlayer, and contains an inorganic system or a metal system ingredient at least as an example of said base material, or the organic – inorganic compound inclination ingredient of this invention is made to intervene as an interlayer, and has a photocatalyst activity ingredient layer and with which the organic system paint film was prepared in the front face can be mentioned preferably.

[0070] Moreover, as an example of goods, the coat layer which contains an inorganic system or a metal system ingredient at least can mention preferably what is the rebound ace court layer containing (1) photocatalyst activity ingredient layer, (2) inorganic system or a metal system conductivity ingredient layer, (3) inorganic system, or a metal system ingredient and (4) inorganic system, a metal system material-for-optical-recording layer, an inorganic system, or a metal system dielectric layer.

[0071] As an application of the organic–inorganic compound inclination ingredient of this invention except for an above-mentioned application — for example, (1) ferroelectric thin film (barium titanate —) The interlayer of UV cut film which consists of interlayer (2) metal vacuum evaporation thin films, such as lead titanate and strontium titanate, (3) The interlayer of the heat ray electric shielding film which consists of a metal vacuum evaporation thin film, the interlayer of the low reflection and the nonreflective coating film which consists of a (4) silica–titania cascade screen, (5) The interlayer of the HUD combiner film which consists of a silica–titania cascade screen, (6) Interlayer for thin films which made the inorganic oxide dope a functional molecule with a sol-gel method (in mineral constituents, such as a silica) A fluorochrome, the coloring matter for laser, a photochromic ingredient, electrochromic materials, The use as film for immobilization to which the chemical bond of the molecules, such as an enzyme, an antibody, and protein, is carried out by the coupling reaction using the under coat the thin film which distributed the nonlinear engineering ingredient, and for the inorganic system antibacterial material for (7) spreading, and the OH radical of the inclination film front face where (8) mineral constituents consist of a silica, [0072] The OH radical of the silica of an inclination film front face is used. (9) A silane system coupling agent and a titanate system coupling agent, The OH radical of the use as reaction sites, such as an aluminates system coupling agent and a zirconate system coupling agent, and the silica of (10) inclination film front face is used. the functional group in which a polymerization is possible is combined — making — the use as a graft reaction place, and **-proof coating (a titania —) of (11) plastics Multiple oxides, such as an alumina, a zirconia and a titania–silica, an alumina–silica, and a zirconia–silica, (12) Heat-resistant coating of plastics, bleed out prevention coating of (13) plastics front face (the bleed out to the front face of the additive in plastics is intercepted), (14) The antioxidizing film on the front face of plastics, the optical fiber which formed the cladding layer which used (15) transparence resin as the core layer by the inclination film, the rod lens which used transparence resin as the rod of a large diameter by (16) same as the above can be mentioned.

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

EXAMPLE

[Example] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples.

[0074] It was made to react at 70 degrees C for 2.5 hours, after mixing formation methyl-methacrylate [product made from Wako Pure Chem Industry] 11.8g of example 1(1) organic-inorganic bipolar membrane, and 3-methacryloxy-propyl-trimethoxysilane [0.5by Shin-Etsu Chemical Co., Ltd.] g and agitating well, adding and agitating 2,2'-azobis isobutyronitrile [product made from Wako Pure Chem Industry] 0.2g to this. After reaction termination, after cooling to a room temperature, the polymerization object was dissolved into 246ml of acetones, 123ml of ethanol was added further, and the solution (a polymer solution is called hereafter.) of the organic high molecular compound of the (A) component was prepared.

[0075] On the other hand, it was dropped into tetra-ethoxy silane [product made from Wako Pure Chem Industry] 61.5ml, agitating a hydrochloric acid and 30.8ml of isopropanol solutions of 0.05g [/ml] hydrochloric-acid concentration, and churning was continued at the room temperature for 5 hours. After dropping this mineral constituent solution calmly into the polymer solution obtained above and agitating it at a room temperature for 4 hours, it diluted with 515ml of acetones, and after churning, it diluted with 738ml of ethanol further, and coating liquid was often prepared. Organic - inorganic bipolar membrane with a thickness of 0.6 micrometers was made to form by applying this coating liquid on a polymethylmethacrylate substrate with a spin coat method (for 1500rpm and 10 seconds), and carrying out stoving processing at 70 degrees C for 12 hours.

[0076] (2) evaluation (**) organic - inorganic bipolar membrane obtained by the lopsidedness above (1) — XPS equipment — using "PHI-5600 [the product made from ULVAC FAI]", argon sputtering (4kV) was performed at intervals of 5 minutes, the film was shaved, the content of the carbon atom on the front face of the film and a silicon atom was measured by X-ray photoelectron spectroscopy, and lopsidedness was investigated. A graph shows relation with the content of sputtering time amount (it is related to the membranous depth), a carbon atom, and a silicon atom to drawing 1. This drawing shows having the outstanding lopsidedness.

[0077] (b) The titanium-dioxide coat film with a thickness of 0.4 micrometers was formed by making into an interlayer organic - inorganic bipolar membrane obtained by the endurance above (1) of a titanium-dioxide interlayer application, applying the photocatalyst coat agent which diluted "STS-01 [the Ishihara Sangyo Kaisha, Ltd. make]" with distilled water 3 times on this with a spin coat method (for 1500rpm and 10 seconds), and carrying out desiccation fixing at 70 degrees C for 12 hours. After putting this in the sealing silica glass container and adjusting to the temperature of 60 degrees C, and 50% of relative humidity, the optical exposure (quantity of light 2.0 mW/cm²) was carried out using the black light, and aging of the permeability in the light (400-800nm) accompanying UV irradiation was measured. Aging of the permeability spectrum of this film in a light field is shown in drawing 12.

[0078] Moreover, from aging of permeability with a wavelength [to UV irradiation time amount] of 500nm, the reduction rate of the permeability was evaluated and this was made into the characteristic of endurance evaluation. A graph shows the relation between UV irradiation days and the decrement of permeability with a wavelength of 500nm to drawing 13. Drawing 12 and drawing 13 show having the outstanding endurance.

[0079] <Accelerated weathering test> Further, the accelerated weathering test was performed for this film using the sunshine weather meter (temperature of 60 degrees C inside the plane, 18 minutes in spray cycle 120 minutes), and change of light transmission and change of an appearance investigated the degree of degradation by the photocatalyst. Change of the visible-ray permeability to the exposure period of a sunshine weather meter is shown in drawing 14. To 90% before a trial, for 20 days, the light transmission of 500nm is maintaining after progress mostly with 87%, and does not have an exterior change, and showed good weatherability.

[0080] Organic-inorganic bipolar membrane was made to form like an example 1 in example 1 except having used the polystyrene substrate instead of the polymethylmethacrylate substrate. About this film, lopsidedness was evaluated like the example 1. A graph shows relation with the content of sputtering time amount, a carbon atom, and a silicon atom to drawing 2. This drawing shows having the outstanding lopsidedness.

[0081] Organic-inorganic bipolar membrane was made to form like an example 1 in example 3 example 1 except having used the polyethylene terephthalate film instead of the polymethylmethacrylate substrate. Lopsidedness was evaluated like the example 1 about this film. A graph shows relation with the content of sputtering time amount, a carbon atom, and a silicon atom to drawing 3. This drawing shows having the outstanding lopsidedness.

[0082] Organic-inorganic bipolar membrane was made to form like an example 1 in example 4 example 1 except having used the polypropylene film instead of the polymethylmethacrylate substrate. Lopsidedness was evaluated like the example 1 about this film. A graph shows relation with the content of sputtering time amount, a carbon atom, and a silicon atom to drawing 4. This drawing shows having the outstanding lopsidedness.

[0083] Organic - inorganic bipolar membrane was made to form like an example 1 in example 5 example 1 except having diluted and used coating liquid 5 times with ethanol / acetone partially aromatic solvent (capacity factors 1/1), and having adopted the dip coating method (a part for 0.5cm/in pull-up rate) instead of the spin coat method. Lopsidedness was evaluated like the example 1 about this film. A graph shows relation with the content of sputtering time amount, a carbon atom, and a silicon atom to drawing 5. This drawing shows having the outstanding lopsidedness.

[0084] Organic-inorganic bipolar membrane was made to form like an example 1 instead of 61.5ml of tetra-ethoxy silanes in example 6 example 1 except having used tetraisopropoxy titanium [product made from Wako Pure Chem Industry] 84.0 ml. Lopsidedness was evaluated like the example 1 about this film. A graph shows relation with the content of sputtering time amount,

a carbon atom, and a titanium atom to drawing 6. This drawing shows having the outstanding lopsidedness.

[0085] Organic-inorganic inclination bipolar membrane was made to form like an example 1 in example 7 example 1 except having used the polycarbonate substrate (the you pyrone made from Mitsubishi Engineering plastics, thickness of 400 micrometers) instead of the polymethylmethacrylate substrate. About this film, lopsidedness was evaluated like the example 1. A graph shows relation with the content of sputtering time amount, a carbon atom, and a silicon atom to drawing 15. This drawing shows having the outstanding lopsidedness.

[0086] An example 8 (1) Formation [of organic-inorganic bipolar membrane] [(A) In the preparation] 100 ml glass container of a component, methyl-methacrylate [product (it may be henceforth written as MMA) made from Wako Pure Chem Industry] 10.92g, and 3-methacryloxy-propyl-trimethoxysilane [Shin-Etsu Chemical Make (it may be henceforth written as MPTMS)] After having put in 2.71g, mixing and agitating well, 2,2'-azobis isobutyronitrile [product made from Wako Pure Chem Industry] 0.2g was added to this, and it sealed by covering to it. The radical polymerization reaction was performed at 70 degrees C for 2.5 hours, having placed this container all over the water bath, and agitating with a magnetic stirrer. After reaction termination, after cooling a polymerization object to a room temperature, 1.0g of polymerization objects was dissolved into 100ml of acetones, and the solution (a polymer solution is called hereafter) of the organic high molecular compound of the (A) component was prepared.

[0087] [(B) preparation of a component] -- on the other hand -- tetra-- it was dropped gradually, agitating the solution which turns into a solution which dissolved ethoxy silane [special grade chemical made from Wako Pure Chem Industry (it may be henceforth written as TEOS)] 12g into 10ml of ethanol from 3.1g of concentrated hydrochloric acid, and 5ml of ethanol. This mixed solution was agitated at the room temperature for 5 hours, and it considered as the mineral constituent solution of the (B) component.

[0088] 10ml of [preparation of inclination film coating liquid] polymer solutions was diluted with 40ml of acetones, 40ml of ethanol was often added after churning, 10ml of mineral constituent solutions was added and agitated further, and inclination film coating liquid was prepared.

[0089] On the rotation cup of a [spin coat of inclination film] spin coater, the polyethylene terephthalate (PET) film [the lumiler T-60 by Toray Industries, Inc. and the film thickness of 188 micrometers] of 12cm angle was fixed, the above-mentioned inclination film coating liquid was carried on the film so that the front face of a film might be wet, the rotation cup was rotated in 1500rpm and 10 seconds after [of since it finishes wetting the whole film] 5 seconds, and the spin coat of the coating liquid was carried out. Organic-inorganic bipolar membrane with a thickness of 0.2 micrometers was made to form on a PET film by carrying out stoving processing of the applied film at 70 degrees C among oven for 12 hours.

[0090] (2) After being immersed in 0.05-N aqueous ammonia for 5 minutes, stoving of the ammoniation above-mentioned film was carried out at 70 degrees C among oven for 12 hours.

[0091] (3) Evaluation [spreading which is a photocatalyst titanium oxide coat agent] The titanium oxide coat film with a thickness of 0.15 micrometers was formed by applying the liquid which diluted the titanium oxide photocatalyst coat agent (Bisto RETA NDC[by Nippon Soda Co., Ltd.]-200C) with isopropanol 10 times with a spin coat method (for 1500rpm and 20 seconds) on this organic-inorganic bipolar membrane, and performing desiccation and heat treatment at 80 degrees C among oven for 12 hours.

[0092] About the film with which coating of the [accelerated weathering test] above-mentioned photocatalyst titanium oxide was carried out, the accelerated weathering test was performed using the sunshine weather meter (temperature of 60 degrees C inside the plane, 18 minutes in spray cycle 120 minutes), and change of light transmission and change of an appearance investigated the degree of degradation by the photocatalyst. Change of the visible-ray permeability to the exposure period of a sunshine weather meter is shown in drawing 16. To 81% before a trial, for 20 days, the light transmission of 500nm is maintaining after progress mostly with 79%, and does not have an exterior change, and showed good weatherability.

[0093] Moreover, when the photocatalyst titanium oxide coat agent was applied like the above about what heat-treated in the autoclave the film coated above (1) on condition that 130 degrees C and 1.7 kgf/cm² for 3 hours and the exposure trial by the sunshine weather meter was performed, the good result was obtained like the ammoniation film.

[0094] In the example 9 [corona discharge treatment of inclination interlayer] example 8, after coating inclination film coating liquid on a PET film [the lumiler T-60 by Toray Industries, Inc., and the film thickness of 188 micrometers], the film with which the coat of the photocatalyst titanium oxide was carried out like the example 8 was obtained except having processed for 3 seconds with the corona discharge processor (Kasuga Electric Works, Ltd. make, applied-voltage 150V, and current 15A). The accelerated weathering test according this film to a sunshine weather meter was performed. Change of the visible-ray permeability to the exposure period of a sunshine weather meter is shown in drawing 17. To 81% before a trial, for 20 days, the light transmission of 500nm is maintaining after progress mostly with 79%, and does not have an exterior change, and showed good weatherability.

[0095] In example 10 example 8, the 10g [/l.] acetone solution of the (A) component was prepared, having used the mole ratio of MMA/MPTMS as 10/1. On the other hand, the TEOS12g and 2.5g [of concentrated hydrochloric acid], and ethanol 5g mixed solution was dropped, and it agitated for 10 hours, and considered as mineral constituent liquid. (A) 3ml and 22ml of acetones of component liquid, and 4ml of mineral constituent liquid were mixed, further, it was easy to add 21ml of n-hexanols, and they were agitated. The PET film was immersed in this liquid, and it pulled up the rate for 15cm/, and coated. The lopsidedness of this coating film was measured like the example 1. The relation between sputtering time amount and the content of a silicon atom is shown in drawing 18. It turns out that it has the lopsidedness which was excellent from this drawing.

[0096] In example 11 example 8, the acetone solution whose (A) component is 10g/l. considering the mole ratio of MMA/MPTMS as 1/1, and 20/1, 100/1 was prepared. On the other hand, the TEOS12g and 2.5g [of concentrated hydrochloric acid], and ethanol 5g mixed solution was dropped, and it agitated for 10 hours, and considered as mineral constituent liquid. (A) 3ml and 22ml of acetones of component liquid, and 4ml of mineral constituent liquid were mixed, further, it was easy to add 21ml of n-hexanols, and they were agitated. The PET film was immersed in this liquid, and it pulled up the rate for 5.0cm/, and coated. The lopsidedness of this coating film was measured like the example 1. drawing 19 -- the three above-mentioned kinds of MMA/MPTMS (mole ratio) -- it attaches and the relation between sputtering time amount and the content of a silicon atom is shown. Change of the mole ratio of MMA/MPTMS shows that the inclination of an inclination is controllable from this drawing.

[0097] In example 12 example 8, the acetone solution whose (A) component is 10g/l. was prepared, having used the mole ratio of MMA/MPTMS as 10/1. On the other hand, the TEOS12g and 2.5g [of concentrated hydrochloric acid], and ethanol 5g mixed solution was dropped, and it agitated for 10 hours, and considered as mineral constituent liquid. (A) The coating liquid arbitrary dose **** and whose mineral constituent concentration are 1, 2, and 4 or 6 % of the weight about mineral constituent liquid was prepared to 1ml and 4ml of acetones of component liquid. The spin coat of this liquid was carried out on the PET film by the same approach as an example 8, and the organic-inorganic compound inclination film was obtained. The lopsidedness of this inclination film was

measured like the example 1. The relation between the sputtering time amount in the inclination film of the four above-mentioned kinds of mineral constituent concentration and the content of a silicon atom is shown in drawing 20. Change of mineral constituent concentration shows that the inclination of an inclination is controllable from this drawing.

[0098] Inclination film coating liquid was coated with the same approach as example 13 example 4 on the automobile steel plate (an acrylic / melanin resin coat) with which the black coating of 3cm angle was applied, and 70 degrees C dried among oven by it for 12 hours. the titanium oxide photocatalyst coat agent (NDC[by Nippon Soda Co., Ltd.]-200C) after processing the obtained automobile steel plate with the film for 3 seconds with plasma jet (PJ[by Kasuga Electric Works, Ltd.]- 1) — what diluted 1g by 0.08g of concentrated hydrochloric acid and 2-propanol 9g was applied with the spin coat method (for 1500rpm and 20 seconds), and the titanium oxide coat film with a thickness of 0.2 micrometers was formed by performing desiccation and heat treatment for 1 hour in [of 80 degrees C] oven. The sunshine weather meter (temperature in a testing machine of 60 degrees C, 18 minutes in spray cycle 120 minutes) performed the accelerated weathering test for the automobile steel plate with which coating of the above-mentioned photocatalyst was carried out, and change of the contact angle of water and an appearance was investigated. When the water contact angle was measured after progress for 20 days, it is less than 3 degrees of contact angles, and was changeless to a surface super-hydrophilic property compared with trial before. Moreover, neither an interference fringe nor milkiness was also seen, but good endurance was shown. The relation between the contact angle of an exposure period and the inclination film and an appearance is shown in Table 1.

[0099] [Table 1]

表 1

		曝 露 時 間 (hr)					
		0	6 0	1 2 0	1 8 0	2 4 0	4 2 0
傾斜膜	接触角(度)	< 3	< 3	< 3	< 3	< 3	< 3
	外 観	良好	良好	良好	良好	良好	良好

[0100] The paint film was made to form like an example 1 in preparation of the polymer solution in example of comparison 1 example 1 except having changed the amount of a methyl methacrylate into 12g, without using 3-methacryloxy propyl trimethoxysilane. Lopsidedness was evaluated like the example 1 about this film. A graph shows relation with the content of sputtering time amount, a carbon atom, and a silicon atom to drawing 7. As shown in this drawing, the film which has lopsidedness was not obtained.

[0101] The paint film was made to form like an example 1 in example of comparison 2 example 1 except having used the glass substrate instead of the polymethylmethacrylate substrate. Lopsidedness was evaluated like the example 1 about this film. A graph shows relation with the content of sputtering time amount, a carbon atom, and a silicon atom to drawing 8. As shown in this drawing, the film which has lopsidedness was not obtained.

[0102] What added acrylic silicone resin solution "GS-1020" [Toagosei 6.5] g of example of comparison 3 marketing to toluene / 20g (capacity factors 1/1) of isopropanol partially aromatic solvents, and carried out churning mixing was applied with the spin coat method (for 1500rpm and 10 seconds) on the polymethylmethacrylate substrate, was dried at 70 degrees C for 12 hours, and the paint film as an interlayer was made to form. About the endurance of the titanium-dioxide interlayer application of this film, it evaluated like the example 1.

[0103] Aging of the permeability spectrum of this film in a light field is shown in drawing 9, and a graph shows the relation between UV irradiation days and the decrement of permeability with a wavelength of 500nm to it at drawing 13. This film did not show good endurance so that drawing 9 and drawing 13 might show.

[0104] What added inorganic adhesive "ethyl silicate 40" [COL Coat 8.1] g of example of comparison 4 marketing to toluene / 20g (capacity factors 1/1) of isopropanol partially aromatic solvents, and carried out churning mixing was applied with the spin coat method (for 1500rpm and 10 seconds) on the polymethylmethacrylate substrate, was dried at 70 degrees C for 12 hours, and the paint film as an interlayer was made to form. About the endurance of the titanium-dioxide interlayer application of this film, it evaluated like the example 1.

[0105] Aging of the permeability spectrum of this film in a light field is shown in drawing 10, and a graph shows the relation between UV irradiation days and the decrement of permeability with a wavelength of 500nm to it at drawing 13. This film did not show good endurance so that drawing 10 and drawing 13 might show.

[0106] Inorganic adhesive "ethyl silicate 40" [COL Coat 1.9] g of marketing was slowly dropped at what added acrylic silicone resin solution "GS-1020" [Toagosei 5.0] g of example of comparison 5 marketing to toluene / 10g (capacity factors 1/1) of isopropanol partially aromatic solvents, and carried out churning mixing, and churning mixing was carried out. Furthermore, toluene / 10g (capacity factors 1/1) of isopropanol partially aromatic solvents were added, churning mixing was carried out, and coating liquid was prepared. This coating liquid was applied with the spin coat method (for 1500rpm and 10 seconds) on the polymethylmethacrylate substrate, was dried at 70 degrees C for 12 hours, and the paint film as an interlayer was made to form. About the endurance of the titanium-dioxide interlayer application of this film, it evaluated like the example 1.

[0107] Aging of the permeability spectrum of this film in a light field is shown in drawing 11, and a graph shows the relation between UV irradiation days and the decrement of permeability with a wavelength of 500nm to it at drawing 13. Although film [this] showed good endurance somewhat, reduction in permeability was too checked, so that drawing 11 and drawing 13 might show.

[0108] In example of comparison 6 example 8, MPTMS was not used but the coating liquid for organic-inorganic bipolar membrane in which the (A) component and the (B) component have not carried out a chemical bond was compounded. Namely, methyl-methacrylate [product made from Wako Pure Chem Industry] 12g and 2,2'-azobis isobutyronitrile [product made from Wako Pure Chem Industry] 0.2g were added in the 50ml glass container, and it sealed by covering. The radical polymerization reaction was performed at 75 degrees C for 2.5 hours, having placed this container all over the water bath, and agitating with a magnetic stirrer. After reaction termination, after cooling a polymerization object to a room temperature, the 0.2g of the above-mentioned polymerization objects was dissolved into 20ml of acetones, and the polymer solution which does not contain MPTMS was prepared.

[0109] On the other hand, the mineral constituent solution of the (B) component was obtained like the example 8 using the tetra-

ethoxy silane. Henceforth, coating liquid is prepared like an example 8, a PET film is coated, and the result of the accelerated weathering test by the sunshine weather meter of the film which applied the photocatalyst titanium oxide coat agent further, and was obtained is shown in drawing 21. As for the light transmission in 500nm, it turned out for 83% before a trial to five days that are after progress, light transmission already fell to 45%, milkiness arose also in the exterior, and the film has deteriorated.

[0110] In example of comparison 7 example 1, the film to which the coat of the photocatalyst titanium oxide was carried out by the same approach as an example 1 was obtained instead of organic-inorganic bipolar membrane coating liquid except having applied the commercial under coat agent for photocatalyst titanium oxide coat agents (Bisto RETA NDC[by Nippon Soda Co., Ltd.]-100A) to the acrylic substrate. The accelerated weathering test according this film to a sunshine weather meter was performed. Change of the visible-ray permeability to the exposure period of a sunshine weather meter is shown in drawing 22. As for the light transmission in 500nm, it turned out for 76% before a trial to five days that are after progress, light transmission already fell to 57%, milkiness arose also in the exterior, and the film has deteriorated.

[0111] In example of comparison 8 example 8, the film to which the coat of the photocatalyst titanium oxide was carried out by the same approach as an example 8 was obtained except having used the commercial under coat agent for photocatalyst titanium oxide coat agents instead of organic-inorganic bipolar membrane coating liquid. The accelerated weathering test according this film to a sunshine weather meter was performed. Change of the visible-ray permeability to the exposure period of a sunshine weather meter is shown in drawing 23. As for the light transmission in 500nm, it turned out for 74% before a trial to 20 days that are after progress, light transmission fell to 66%, milkiness arose also in the exterior, and the film has deteriorated.

[0112] It was made to react at 70 degrees C for 2.5 hours, after mixing example 14 [(A) Preparation of component] methyl methacrylate 21.8g, and 3-methacryloxy-propyl-trimethoxysilane 5.41g and agitating well, adding and agitating 2,2'-azobis isobutyronitrile 0.4g to this. 4g of the obtained polymerization object was dissolved in the 2l. methyl ethyl ketone after radiational cooling, and the polymer solution of the (A) component was prepared.

[0113] It was slowly dropped into [(B) Preparation of component] one side, and a mixed solution (tetra-ethoxy silane 480g and ethanol 400g), agitating the mixed liquor of 40g of concentrated nitric acid, ethanol 200g, and 460g of water, churning was continued at the room temperature for 5 hours, and it considered as the mineral constituent solution of the (B) component.

[0114] [Preparation of inclination film coating liquid]
 (A) 1.5l. of ethylcellosolve was added to the polymer solution of a component, after carrying out churning mixing, 500g of mineral constituent solutions of the (B) component was added to this, it agitated well, and inclination film coating liquid was prepared.

[0115] Coating was carried out to the PET film "lumiler T-60" (thickness of 50 micrometers, width of face of 330mm) by Toray Industries [, Inc.], Inc., and organic-inorganic bipolar membrane with a thickness of 0.1 micrometers was made to form by the KISUMA year bar method (0.1mm of wire sizes, line speed 10 m/min, drying temperature of 120 degrees C) by the "multi-coating machine M200" by [bar coat of inclination film] Hirano Tecseed. Lopsidedness was evaluated like the example 1 about this film. Relation with the content of sputtering time amount, a carbon atom, and a silicon atom is shown in a graph at drawing 24. It turns out that it has the lopsidedness which was excellent from this drawing.

[0116] 2g of the polymerization object obtained like example 15 example 14 was dissolved in 1l. methyl isobutyl ketone, and it considered as the polymer solution of the (A) component. 0.8l. of 1-butanol was added, after carrying out churning mixing, to this polymer solution, 200g of mineral constituent solutions of the (B) component in an example 14 was added, it agitated well to it, and inclination film coating liquid was prepared to it.

[0117] Coating of this was carried out to the acrylic board "a bitter taste rewrite" (thickness of 2mm, 300mmx300mm) by the Mitsubishi Rayon company with the Anest Iwata spray gun "W-88 series" in Ayr ** 0.2MPa, the spray distance of 15cm, and spray operating-speed 15 m/min, desiccation processing was carried out at 80 degrees C, and organic-inorganic ***** with a thickness of 0.15 micrometers was made to form. Lopsidedness was evaluated like the example 1 about this film. Relation with the content of sputtering time amount, a carbon atom, and a silicon atom is shown in a graph at drawing 25. It turns out that it has the lopsidedness which was excellent from this drawing.

[0118] the inside of the polymerization object obtained like example 16 example 14, and 1g — the Matsumoto Chemical Industry Co., Ltd. make — tetra — isocyanato "ORUGACHIKKUSU-silane Si 400" 56g was dissolved in 1l. toluene, and inclination film coating liquid was prepared.

[0119] Coating of this was carried out to the acrylic board "a bitter taste rewrite" (thickness of 2mm, 300mmx300mm) by the Mitsubishi Rayon company with the Anest Iwata spray gun "W-88 series" in Ayr ** 0.2MPa, the spray distance of 15cm, and spray operating-speed 15 m/min, desiccation processing was carried out at 25 degrees C, and organic-inorganic ***** with a thickness of 0.12 micrometers was made to form. Lopsidedness was evaluated like the example 1 about this film. Relation with the content of sputtering time amount, a carbon atom, and a silicon atom is shown in a graph at drawing 26. It turns out that it has the lopsidedness which was excellent from this drawing.

[0120] the inside of the polymerization object obtained like example 17 example 14, and 1g — the TONEN CORP. make — polysilazane "L110 (20-% of the weight xylene solution)" 0.29 l. was dissolved in the 0.71l. xylene, and inclination film coating liquid was prepared.

[0121] Coating of this was carried out to the PET film "the east rel mirror T-60" in the spin coater (1500rpm, 15 seconds), desiccation processing was carried out by 95 degrees C and 80%RH at 80 degrees C for 3 hours for 1 hour, and organic-inorganic ***** with a thickness of 0.12 micrometers was made to form. Lopsidedness was evaluated like the example 1 about this film. Relation with the content of sputtering time amount, a carbon atom, and a silicon atom is shown in a graph at drawing 27. It turns out that it has the lopsidedness which was excellent from this drawing.

[0122] example 18 [(A) preparation of component] styrene (Wako Pure Chem industry) 11.86g, and 3-methacryloxy-propyl-trimethoxysilane 1.42g — glassware with a capacity of 50ml — putting in — 2,2'-azobis isobutyronitrile 0.2g — in addition, it agitated and was made to dissolve completely Next, with the water bath adjusted to 70 degrees C, this container was heated for 5 hours and the polymerization of the styrene was carried out. Moved 0.2mg of obtained polystyrene copolymers to another glassware, it was made to dissolve in 200ml of tetrahydrofuran solvents, and the polymer solution of the (A) component was prepared.

[0123] 40ml of tetrahydrofurans and 40ml of ethanol were put into glassware with a [preparation of inclination film] capacity of 100ml, and, in addition, it prepared inclination film coating liquid the above-mentioned polymer solution and 10ml of mineral constituent solutions at a time obtained in the example 1 to this.

[0124] It applies on a PET substrate with a spin coat method, and it was made to dry and organic-inorganic bipolar membrane was made to form by the approach according to an example 1 using the [spin coat of inclination film] above-mentioned coating liquid.

Lopsidedness was evaluated like the example 1 about this film. Relation with the content of sputtering time amount, a carbon atom, and a silicon atom is shown in a graph at drawing 28. It turns out that it has the lopsidedness which was excellent from this drawing.

[0125] Example 19 It was made to react at 75 degrees C for 3 hours, after being easy to mix and agitating formation methyl methacrylate 10.92g of conductive film (1) organic-inorganic bipolar membrane, and 3-methacryloxy-propyl-trimethoxysilane 2.71g, adding and agitating 2,2'-azobis isobutyronitrile 0.2g to this. 1.0g of the obtained polymerization object was dissolved in 100ml of acetones, and the solution (a polymer solution is called hereafter.) of the organic high molecular compound of the (A) component was prepared.

[0126] It was dropped gradually, agitating the solution which, on the other hand, turns into a solution which dissolved tetra-ethoxy silane 12g in 10ml of ethanol from 3.1g of concentrated hydrochloric acid, and 5ml of ethanol. This mixed solution was agitated at the room temperature for 5 hours, and the mineral constituent solution of the (B) component was obtained. 40ml of ethanol was added, and after mixing 10ml of polymer solutions to 40ml of acetones and agitating to homogeneity, further, 10ml of mineral constituents was added, and it agitated until it became homogeneity.

[0127] Organic - inorganic bipolar membrane was made to form on a substrate, when this coating liquid is applied with a spin coat method (1500rpm, 10 seconds) on the polyethylene terephthalate film whose thickness is 0.188mm and carries out stoving at 40 degrees C for 12 hours. By depth profile measurement of XPS (the product made from ULVAC FAI, PHI-5600) of this film, the content ratio of carbon and silicon was measured and lopsidedness was investigated. A graph shows relation with the content of sputtering time amount, a carbon atom, and a silicon atom to drawing 29. It turns out that it has the lopsidedness which was excellent from this drawing.

[0128] (2) On the film obtained by production (1) of a conductive film, using the oxide target which consists of 90 % of the weight of indium oxide, and 10 % of the weight of stannic oxides, the transparence electric conduction film with a thickness of 40nm was made to form with DC magnetron sputtering equipment (Shimadzu, HS-720), and the conductive film was produced under the mixed-gas (it is 99:1 at volume ratio) ambient atmosphere of an argon and oxygen. Sheet resistance, light transmission, the squares friction test, and the heat test were investigated according to the following approaches using the obtained conductive film as the property. The result was summarized in Table 2.

[0129] (b) The transparence electric conduction film sheet resistance (Ω/\square) formed in sheet resistance one side was measured using the resistivity meter.

(b) The light transmission spectrophotometer (Shimadzu, UV-2100) was and the light transmission (%) of 550nm was measured.

(c) The squares tape method was enforced according to the squares friction test JIS K5400. After making 100 mass attachment and the Nichiban Scotch tape (trademark) stick the squares of 1mm angle to the paint film side of each test piece by pressure in a rotary cutter, 180 friction tests were carried out at the rate of 800 mm/min. Adhesion was evaluated by counting the existence of exfoliation among 100 masses.

[0130] (d) The temperature was lowered after 2-hour maintenance at 70 degrees C in oven, having heat resistance test applied it to -30 degrees C for 2 hours, and after that, it held at -30 degrees C for 2 hours, and 5 cycle **** and a thermo-cycle trial were carried out for the process which carries out a temperature up over 2 hours to 70 degrees C again. Measurement and the squares friction test of sheet resistance performed evaluation by checking the adhesion (existence of exfoliation in 100 masses) of a paint film.

[0131] The conductive film was produced by the same approach as an example 19 to the polycarbonate film with the organic-inorganic compound inclination film obtained in the example 20 example 7. The property of this conductive film is shown in Table 2.

[0132] It was dropped gradually, agitating the solution which turns into a solution which dissolved example 21 tetra-ethoxy silane 8.33g and methyl trimethoxysilane 1.36g in 10ml of ethanol from 3.1g of concentrated hydrochloric acid, and 5ml of ethanol. This mixed solution was agitated at the room temperature for 5 hours, and the mineral constituent solution was obtained.

[0133] After mixing 10ml of (A) polymer solutions of an example 19 to 40ml of acetones and agitating to homogeneity, 40ml of ethanol was added, further, 10ml of mineral constituent solutions was added, and the conductive film was completely produced by this actuation with the example 19 except having agitated until it became homogeneity.

[0134] By depth profile measurement of XPS (the product made from ULVAC FAI, PHI-5600) of organic-inorganic bipolar membrane before coating drawing 30 with the ITO film, the content ratio of carbon and silicon was measured and the result of having investigated lopsidedness was indicated. The property of this conductive film is shown in Table 2.

[0135] In example of comparison 9 example 19, adding and agitating 2,2'-azobis isobutyronitrile 0.2g to methyl methacrylate 12g, it was made to react at 75 degrees C for 3 hours, and 1.0g of the obtained polymerization object was dissolved in 100ml of acetones, except having prepared the solution of a polymethylmethacrylate compound, this actuation was completely performed with the example 19, and the conductive film was produced.

[0136] By depth profile measurement of XPS (the product made from ULVAC FAI, PHI-5600) of organic-inorganic bipolar membrane before coating drawing 31 with the ITO film, the content ratio of carbon and silicon was measured and the result of having investigated lopsidedness was indicated. The property of this conductive film is shown in Table 2.

[0137] The conductive film was completely produced by this actuation with the example 19 except having diluted with 20ml of acetones, and 20ml of ethanol 10ml of solutions of the polymethylmethacrylate compound prepared in the example 9 of example of comparison 10 comparison, and having considered as coating liquid. The property of this conductive film is shown in Table 2.

[0138]

[Table 2]

表2

	導電性フィルムの特性				
	シート抵抗 (Ω/\square)	光線 透過率 (%)	基盤目 剥離試験	耐熱性	
				シート抵抗 (Ω/\square)	基盤目 剥離試験
実施例 19	300	85	94/100	320	92/100
実施例 20	280	83	100/100	280	100/100
実施例 21	280	85	95/100	280	93/100
比較例 9	310	84	50/100	1300	40/100
比較例 10	300	85	100/100	1850	35/100

[0139] Although conductivity and adhesion hardly change the conductive film of an example using the compound inclination film of this invention as an interlayer after a heat test as shown in Table 2, as for the thing of the example of a comparison, conductivity and adhesion are falling greatly after a heat test.

[0140] Example 22 In the rebound ace court film example 8, except having replaced the base material film with the polycarbonate film, it is the same approach as an example 8, and the film with the organic-inorganic compound inclination film was obtained. To this, the silicon rebound ace court agent made from Japanese DAKUROSHAMU Lock [the sol guard NP730] was formed using the bar coating machine so that the thickness after desiccation might be set to 4 micrometers, hardening processing of 2 hours was performed at 80 degrees C after that, and the desired base material with the rebound ace court film was obtained. In addition, when the pencil degree of hardness was measured about the film in front of a rebound ace court, only the polycarbonate film was H with the film which prepared F and the compound inclination film. The following trials were carried out about this base material with the rebound ace court film. The result was summarized in Table 3.

[0141] (1) Adhesion JIS The squares tape method was enforced according to K5400. After making 100 mass attachment and the Nichiban Scotch tape stick the squares of 1mm angle to the paint film side of each test piece by pressure in a rotary cutter, 180 friction tests were carried out at the rate of 300 mm/min. Adhesion was evaluated by counting the existence of exfoliation among 100 masses.

[0142] (2) Film degree of hardness JIS According to K5400, the pencil hardness test was carried out with reed MITSU Seiki Co., Ltd. make and a pencil scrape test machine, and the existence of the blemish of a paint film estimated the film degree of hardness.

[0143] (3) The antifriction trial of a paint film was carried out with wear-resistant reed MITSU Seiki Co., Ltd. make and a taper type abrasion tester (test condition: 200 counts of wear, 500g of loads, wear ring CS-10F). Whenever [after a trial / cloudiness] (Hayes value: deltaH%) estimated abrasion resistance.

[0144] (4) The temperature was lowered after 2-hour maintenance at 70 degrees C in oven, having heat resistance test applied it to -30 degrees C for 2 hours, and after that, it held at -30 degrees C for 2 hours, and 5 cycle **** and a thermo-cycle trial were carried out for the process which carries out a temperature up over 2 hours to 70 degrees C again. Evaluation was performed by checking the adhesion (existence of exfoliation in 100 masses) of a paint film by the squares tape method.

[0145] The base material with the rebound ace court film was obtained by the completely same actuation as an example 22 except having changed into the film (example 23) which carried out the coat of the inclination film at the polyethylene terephthalate film with a thickness of 0.188mm which produced an example 23 and 24 substrates in the example 19 from the polycarbonate film with a thickness of 0.4mm, and the acrylic film (example 24) with a thickness of 0.2mm. The evaluation result of this base material with the film was summarized in Table 3. About the film of an example 24, the content ratio of carbon and silicon was measured to drawing 32, lopsidedness was investigated to it, and the result was indicated to it by depth profile measurement of XPS (the product made from ULVAC FAI, PHI-5600) of the film in front of hard coating.

[0146] In addition, the pencil degrees of hardness of the film which prepared the compound inclination film in a polyethylene terephthalate film and it were 3H and 4H, respectively, and the pencil degrees of hardness of the film which prepared the compound inclination film in an acrylic film and it were 4H and 5H, respectively.

[0147] After mixing 10ml of polymer solutions of the (A) component of an example 8 to 40ml of example 25 acetones and agitating to homogeneity, 30ml of ethanol was added, further, 20ml of mineral constituent solutions of the (B) component of an example 8 was added, and it agitated until it became homogeneity, and the substrate with the rebound ace court film was completely obtained by the same actuation as an example 8 except having replaced the film base material with the polycarbonate film further. The evaluation result of this base material with the film was summarized in Table 3. By depth profile measurement of XPS (the product made from ULVAC FAI, PHI-5600) of the film in front of a rebound ace court, the content ratio of carbon and silicon was measured to drawing 33, lopsidedness was investigated to it, and the result was indicated to it.

[0148] Adding and agitating 2,2'-azobis isobutyronitrile 0.2g to methyl methacrylate 12g in example of comparison 11 example 8, it was made to react at 75 degrees C for 3 hours, and except having dissolved 1.0g of the obtained polymerization object in 100ml of acetones, having prepared the solution of a polymethylmethacrylate compound, having considered as the polymer solution, and having used the film base material as the polycarbonate film, this actuation was completely performed with the example 8, and the base material with the rebound ace court film was produced. Table 3 was asked for the evaluation result of this base material with the film.

[0149] On the polycarbonate film with an example of comparison 12 thickness of 0.4mm, the silicon rebound ace court agent made from Japanese DAKUROSHAMU Lock [the sol guard NP730] was formed in the bar coating machine so that the thickness after desiccation might be set to 4 micrometers, on it, hardening processing of 2 hours was performed at 80 degrees C after that, and the desired base material with the rebound ace court film was obtained on it. The evaluation result of this base material with the film was summarized in Table 3.

[0150]

[Table 3]

表 3

	密 着 性	膜 硬 度	耐 摩 耗 性 ($\Delta H\%$)	耐 熱 性
実施例 2 2	100/100	4 H	8	100/100
実施例 2 3	94/100	6 H	8	92/100
実施例 2 4	100/100	6 H	6	100/100
実施例 2 5	100/100	4 H	8	100/100
比較例 1 1	44/100	3 H	28	34/100
比較例 1 2	10/100	2 H	55	0/100

[0151] As shown in Table 3, when the inclination film is used as a primer of a rebound ace court layer (examples 22-25), since it has inclination structure, inclination covering it from a mineral constituent into the structure at an organic component including a mineral constituent and an organic component, it is extremely excellent in the adhesive property of an organic base material and the both sides of a silicon system rebound ace court layer, and may fully demonstrate the engine performance of a rebound ace court layer.

[0152] On the other hand, since the mineral constituent and the organic component have not carried out a chemical bond when the acrylic silicone which does not have a chemical bond is used as a primer layer of a rebound ace court layer between the methyl methacrylate polymer of the (A) component, and the mineral constituent of the (B) component (example 11 of a comparison), it does not become inclination structure, but the adhesion of the interface of a mineral constituent and an organic component is low, and inferior to the engine performance. Moreover, since the rebound ace court agent itself is the silicon system of an inorganic material when there is no primer (example 12 of a comparison), it is lacking in adhesion with an organic base material, and inferior to the engine performance.

[0153] Example 26 The polycarbonate film with the inclination film obtained in the optical-recording-medium example 7 was set in the sputtering system, the SiN layer with a thickness of 8 micrometers was formed as a dielectric substrate layer (under coat) on the inclination film, and the under coat formation resin substrate was obtained. The desired magneto-optic-recording medium was obtained by setting an under coat formation resin substrate in a sputtering system, forming a TbDyFeCo layer with a thickness of 10 micrometers as a magneto-optic-recording layer on an under coat, and forming a SiN layer with a thickness of 8 micrometers as a dielectric protective layer (topcoat) further. The following trials were carried out about this magneto-optic-recording medium. The result was summarized in Table 4.

[0154] (1) Adhesion JIS between an under coat and a base material film The squares tape method was enforced according to K5400. After making 100 mass attachment and the Nichiban Scotch tape stick the squares of 1mm angle to the paint film side of each test piece by pressure in a rotary cutter, 180 friction tests were carried out at the rate of 300 mm/min. Adhesion was evaluated by counting the existence of exfoliation among 100 masses. Moreover, the temperature was lowered after 2-hour maintenance at 70 degrees C in oven, having covered it over -30 degrees C for 2 hours, and after that, it held at -30 degrees C for 2 hours, and 5 cycle **** and a thermo-cycle trial were carried out for the process which carries out a temperature up over 2 hours to 70 degrees C again, and adhesion was measured similarly.

[0155] (2) Film degree of hardness JIS According to K5400, the pencil hardness test was carried out with reed MITSU Seiki Co., Ltd. make and a pencil scrape test machine, and the existence of the blemish of a paint film estimated the film degree of hardness.

[0156] After mixing 10ml of polymer solutions of the (A) component of an example 19 to 40ml of example 27 acetones and agitating to homogeneity, 30ml of ethanol was added, further, 20ml of mineral constituent solutions of the (B) component of an example 19 was added, and the magneto-optic-recording medium was completely obtained by the same actuation as an example 19 except the actuation agitated until it became homogeneity. The evaluation result of this base material with the film was summarized in Table 4.

[0157] It kept at 75 degrees C, mixing and agitating example of comparison 13 methyl methacrylate 12g, and azobisisobutyronitril 0.2g, and the magneto-optic-recording medium was obtained by the same actuation as an example 26 except having made it react for 3 hours and having obtained the organic macromolecule component. The property of this magneto-optic-recording medium is shown in Table 4.

[0158] The magneto-optic-recording medium was created by the example 26 and this technique, without forming organic-inorganic bipolar membrane in an example of comparison 14 polycarbonate substrate. The property of this magneto-optic-recording medium is shown in Table 4.

[0159]

[Table 4]

表 4

	アンダーコートと樹脂基板との密着性		膜 硬 度
	ヒートサイクル前	ヒートサイクル後	
実施例 2 6	100/100	95/100	H
実施例 2 7	100/100	94/100	H
比較例 1 3	81/100	65/100	H
比較例 1 4	0/100	0/100	F

[0160] In addition, the curvature of each substrate after holding under the high-humidity/temperature of 70 degrees C and 90%RH for 40 hours was measured, and when it investigated whether there would be any trouble in the writing and readout of data, the problem did not have both examples 26 and 27 and the examples 13 and 14 of a comparison.

[Translation done.]

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2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

- [Drawing 1] It is the graph which shows relation with the content of the sputtering time amount in organic-inorganic bipolar membrane obtained in the example 1, a carbon atom, and a silicon atom.
- [Drawing 2] It is the graph which shows relation with the content of the sputtering time amount in organic-inorganic bipolar membrane obtained in the example 2, a carbon atom, and a silicon atom.
- [Drawing 3] It is the graph which shows relation with the content of the sputtering time amount in organic-inorganic bipolar membrane obtained in the example 3, a carbon atom, and a silicon atom.
- [Drawing 4] It is the graph which shows relation with the content of the sputtering time amount in organic-inorganic bipolar membrane obtained in the example 4, a carbon atom, and a silicon atom.
- [Drawing 5] It is the graph which shows relation with the content of the sputtering time amount in organic-inorganic bipolar membrane obtained in the example 5, a carbon atom, and a silicon atom.
- [Drawing 6] It is the graph which shows relation with the content of the sputtering time amount in organic-inorganic bipolar membrane obtained in the example 6, a carbon atom, and a titanium atom.
- [Drawing 7] It is the graph which shows relation with the content of the sputtering time amount in the paint film obtained in the example 1 of a comparison, a carbon atom, and a silicon atom.
- [Drawing 8] It is the graph which shows relation with the content of the sputtering time amount in the paint film obtained in the example 2 of a comparison, a carbon atom, and a silicon atom.
- [Drawing 9] It is the graph which shows aging of the permeability spectrum in the light field in the paint film obtained in the example 3 of a comparison.
- [Drawing 10] It is the graph which shows aging of the permeability spectrum in the light field in the paint film obtained in the example 4 of a comparison.
- [Drawing 11] It is the graph which shows aging of the permeability spectrum in the light field in the paint film obtained in the example 5 of a comparison.
- [Drawing 12] It is the graph which shows aging of the permeability spectrum in the light field in organic-inorganic bipolar membrane obtained in the example 1.
- [Drawing 13] It is the graph which shows relation with the decrement of with a wavelength [in the paint film obtained in organic-inorganic bipolar membrane and the examples 3-5 of a comparison which were acquired in the example 1 / the UV irradiation days and wavelength of 500nm] permeability.
- [Drawing 14] It is the graph which shows change of the visible-ray permeability in the exposure trial of the sunshine weather meter of the film with which organic-inorganic bipolar membrane was made into the interlayer, and the titanium-dioxide coat film was prepared obtained in the example 1.
- [Drawing 15] It is the graph which shows relation with the content of the sputtering time amount in organic-inorganic bipolar membrane obtained in the example 7, a carbon atom, and a silicon atom.
- [Drawing 16] It is the graph which shows change of the visible-ray permeability in the exposure trial of the sunshine weather meter of the film with which organic-inorganic bipolar membrane was made into the interlayer, and the titanium-dioxide coat film was prepared obtained in the example 8.
- [Drawing 17] It is the graph which shows change of the visible-ray permeability in the exposure trial of the sunshine weather meter of the film with which organic-inorganic bipolar membrane was made into the interlayer, and the titanium-dioxide coat film was prepared obtained in the example 9.
- [Drawing 18] It is the graph which shows relation with the content of the sputtering time amount in organic-inorganic bipolar membrane obtained in the example 10, a carbon atom, and a silicon atom.
- [Drawing 19] It is the graph which shows the relation between the sputtering time amount in three kinds of organic-inorganic bipolar membrane obtained in the example 11, and the content of a silicon atom.
- [Drawing 20] It is the graph which shows the relation between the sputtering time amount in four kinds of organic-inorganic bipolar membrane obtained in the example 12, and the content of a silicon atom.
- [Drawing 21] It is the graph which shows change of the visible-ray permeability in the exposure trial of the sunshine weather meter of the film with which organic-inorganic bipolar membrane was made into the interlayer, and the titanium-dioxide coat film was prepared obtained in the example 6 of a comparison.
- [Drawing 22] It is the graph which shows change of the visible-ray permeability in the exposure trial of the sunshine weather meter of the film with which the under coat agent was made into the interlayer, and the titanium-dioxide coat film was prepared obtained in the example 7 of a comparison.
- [Drawing 23] It is the graph which shows change of the visible-ray permeability in the exposure trial of the sunshine weather meter of the film with which the under coat agent was made into the interlayer, and the titanium-dioxide coat film was prepared obtained in the example 8 of a comparison.
- [Drawing 24] It is the graph which shows relation with the content of the sputtering time amount in organic-inorganic bipolar membrane obtained in the example 14, a carbon atom, and a silicon atom.
- [Drawing 25] It is the graph which shows relation with the content of the sputtering time amount in organic-inorganic bipolar membrane obtained in the example 15, a carbon atom, and a silicon atom.

[Drawing 26] It is the graph which shows relation with the content of the sputtering time amount in organic-inorganic bipolar membrane obtained in the example 16, a carbon atom, and a silicon atom.

[Drawing 27] It is the graph which shows relation with the content of the sputtering time amount in organic-inorganic bipolar membrane obtained in the example 17, a carbon atom, and a silicon atom.

[Drawing 28] It is the graph which shows relation with the content of the sputtering time amount in organic-inorganic bipolar membrane obtained in the example 18, a carbon atom, and a silicon atom.

[Drawing 29] It is the graph which shows relation with the content of the sputtering time amount in organic-inorganic bipolar membrane obtained in the example 19, a carbon atom, and a silicon atom.

[Drawing 30] It is the graph which shows relation with the content of the sputtering time amount in organic-inorganic bipolar membrane obtained in the example 21, a carbon atom, and a silicon atom.

[Drawing 31] It is the graph which shows relation with the content of the sputtering time amount in organic - inorganic bipolar membrane obtained in the example 9 of a comparison, a carbon atom, and a silicon atom.

[Drawing 32] It is the graph which shows relation with the content of the sputtering time amount in organic-inorganic bipolar membrane obtained in the example 24, a carbon atom, and a silicon atom.

[Drawing 33] It is the graph which shows relation with the content of the sputtering time amount in organic-inorganic bipolar membrane obtained in the example 25, a carbon atom, and a silicon atom.

[Translation done.]

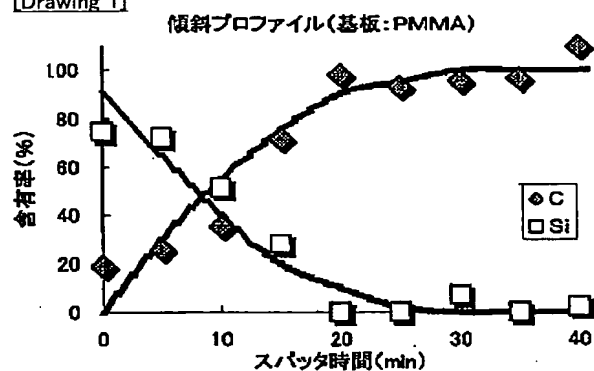
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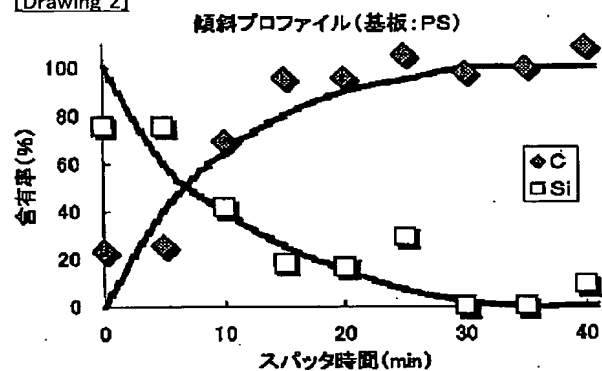
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2. **** shows the word which can not be translated.
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DRAWINGS

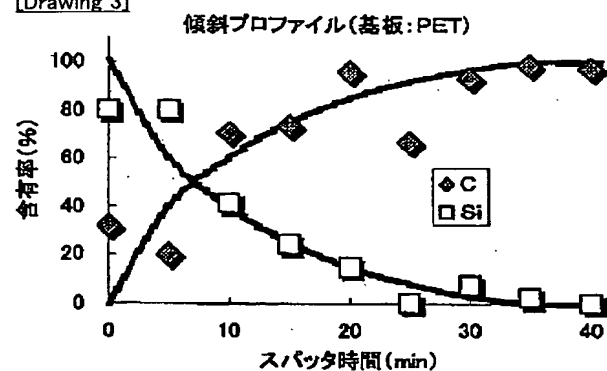
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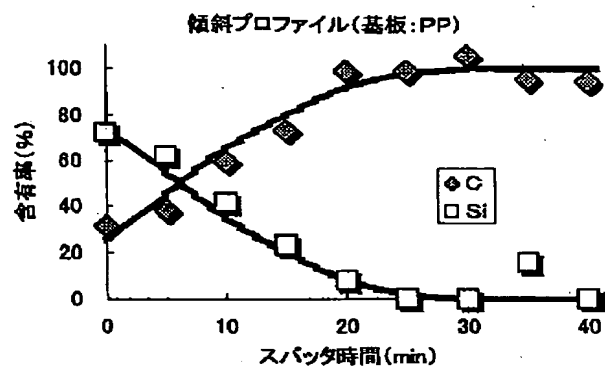
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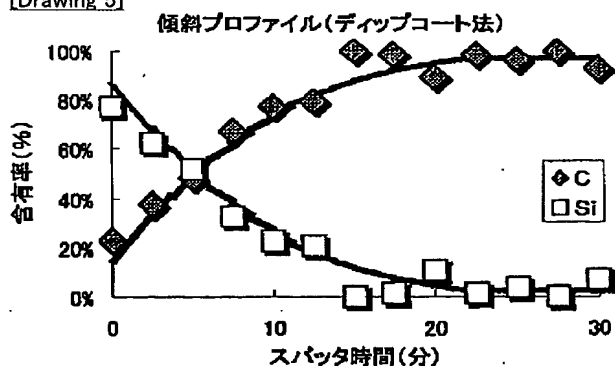
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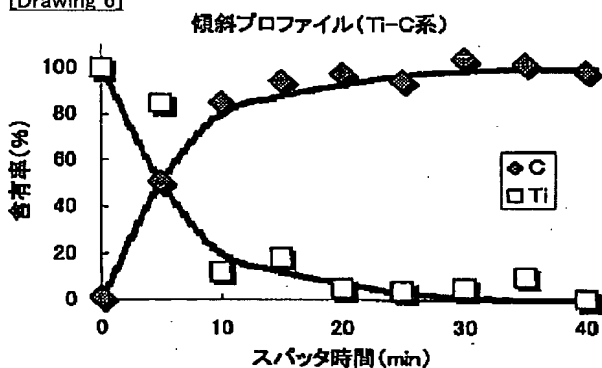
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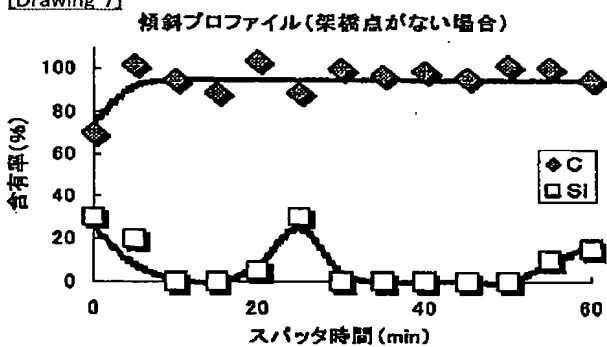
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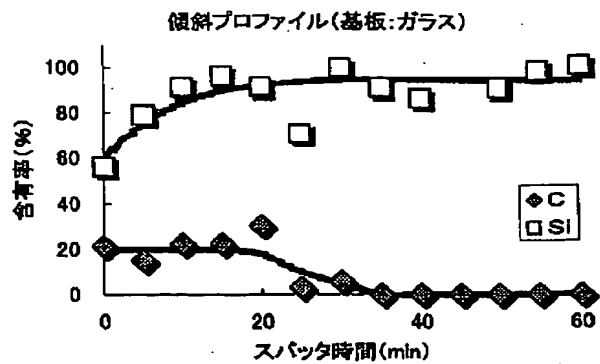
[Drawing 6]



[Drawing 7]

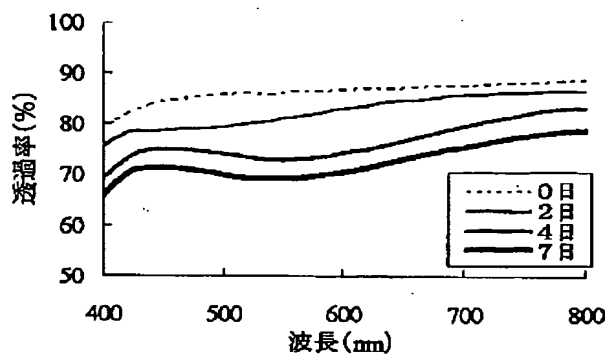


[Drawing 8]



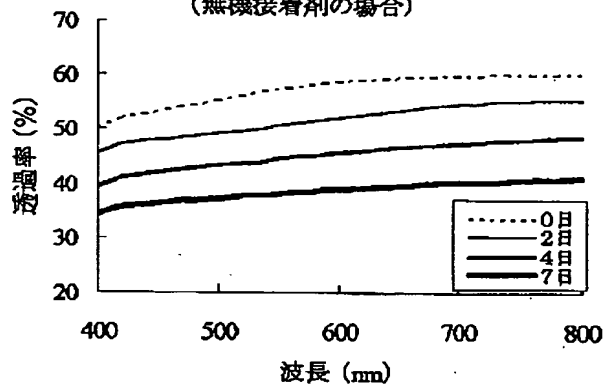
[Drawing 9]

UV照射に伴う透過率の減少
(有機接着剤の場合)



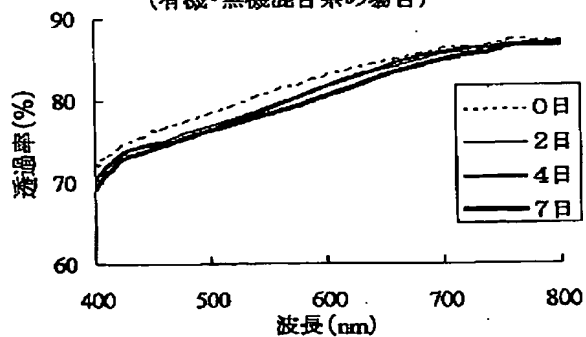
[Drawing 10]

UV照射に伴う透過率の減少
(無機接着剤の場合)



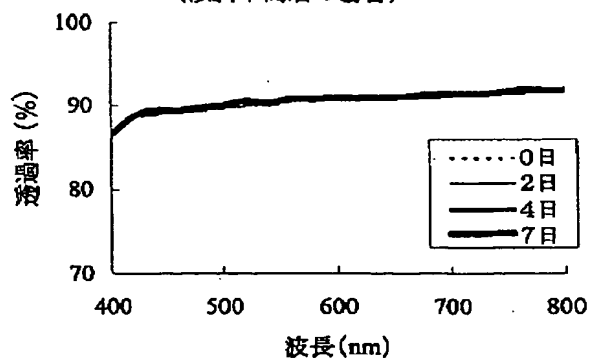
[Drawing 11]

UV照射に伴う透過率の減少
(有機・無機混合系の場合)



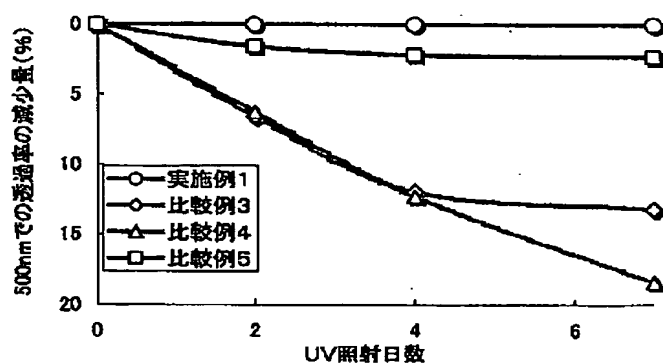
[Drawing 12]

UV照射時の透過率の減少
(傾斜中間層の場合)



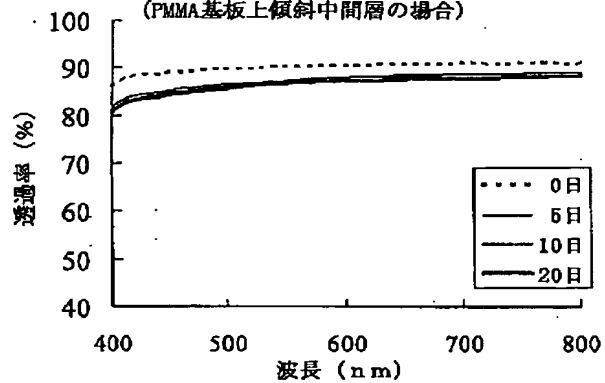
[Drawing 13]

UV照射に伴う透過率の経時変化



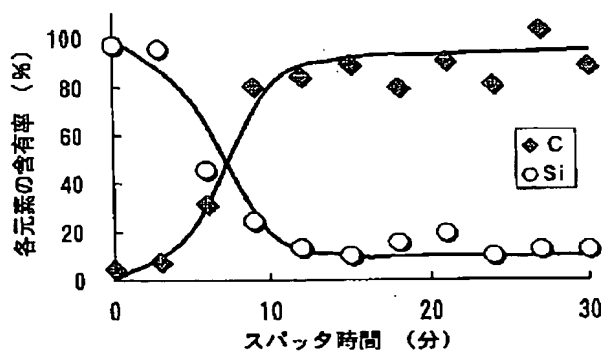
[Drawing 14]

サンシャインエサ-マー試験における透過率の減少
(PMMA基板上傾斜中間層の場合)

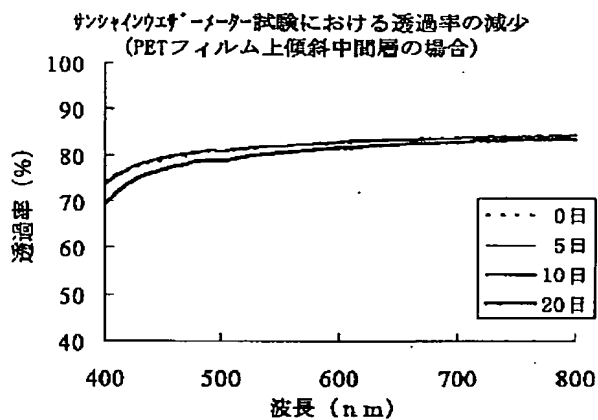


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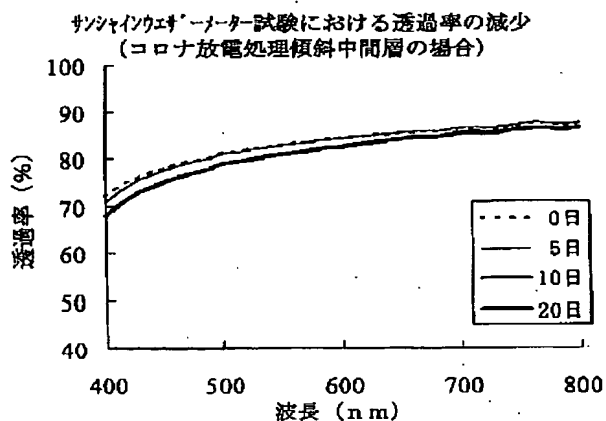
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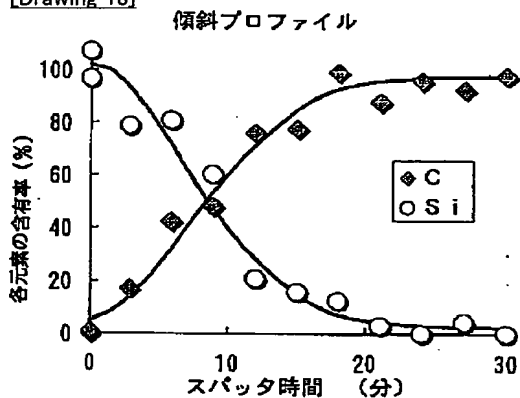
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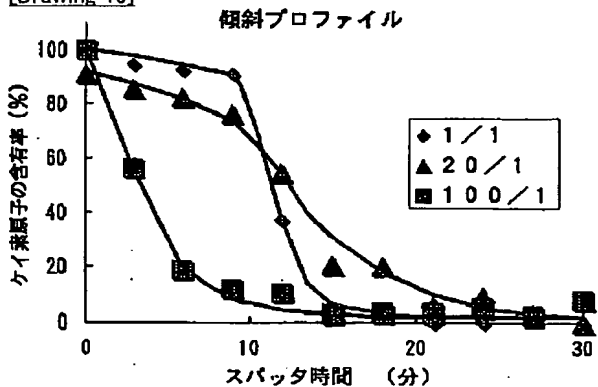
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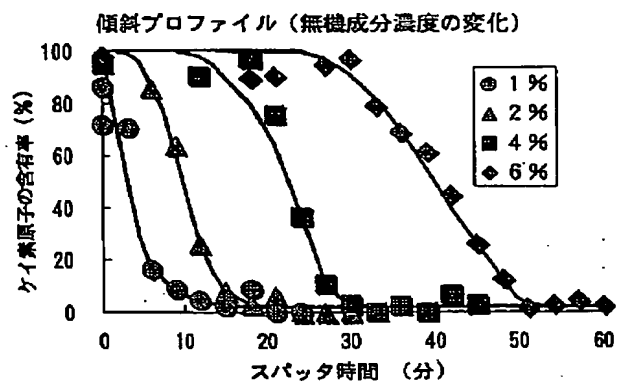
[Drawing 18]



[Drawing 19]

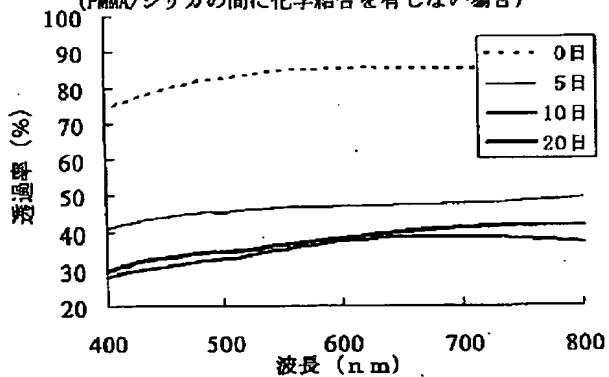


[Drawing 20]



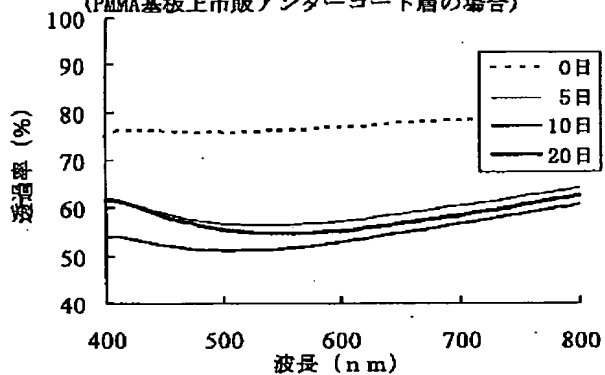
[Drawing 21]

サンシャインウェーバー試験における透過率の減少
(PMMA/シリカの間に化学結合を有しない場合)



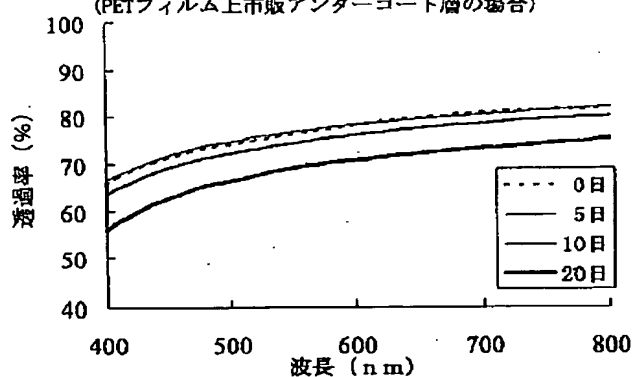
[Drawing 22]

サンシャインウェーバー試験における透過率の減少
(PMMA基板上市販アンダーコート層の場合)

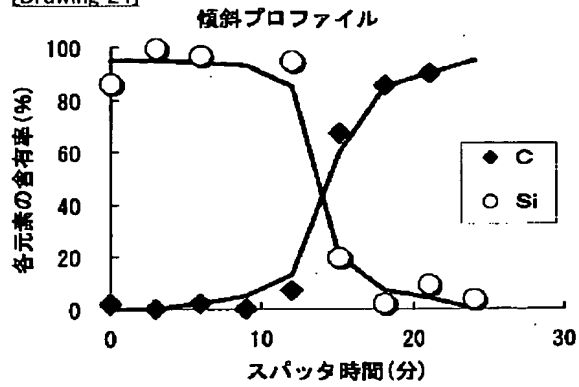


[Drawing 23]

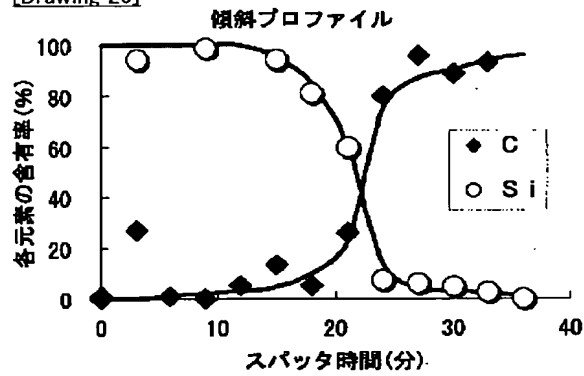
サンシャインウェーバー試験における透過率の減少
(PETフィルム上市販アンダーコート層の場合)



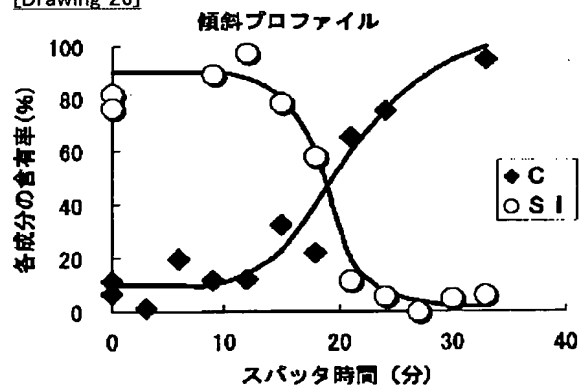
[Drawing 24]



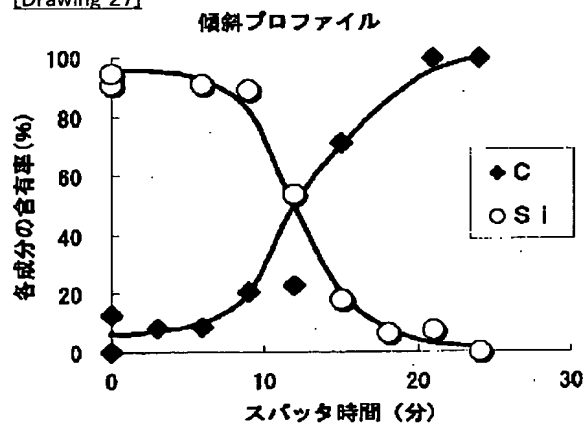
[Drawing 25]



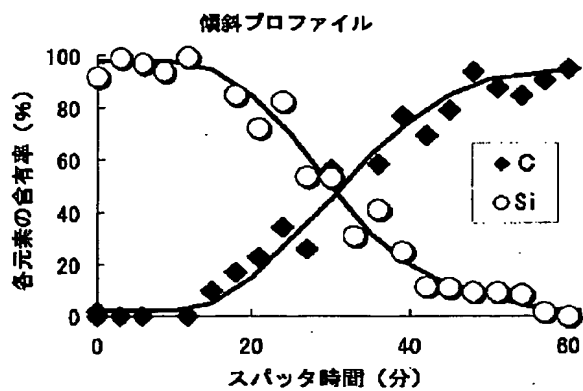
[Drawing 26]



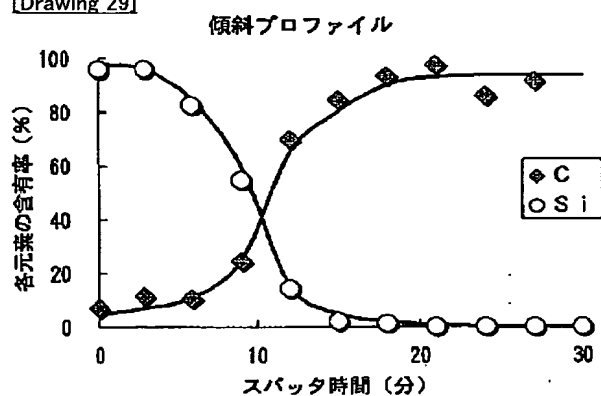
[Drawing 27]



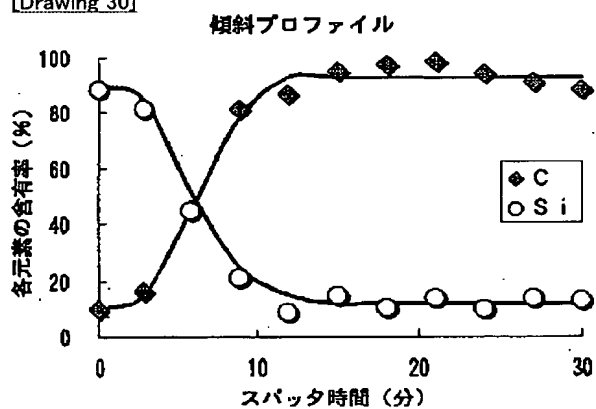
[Drawing 28]



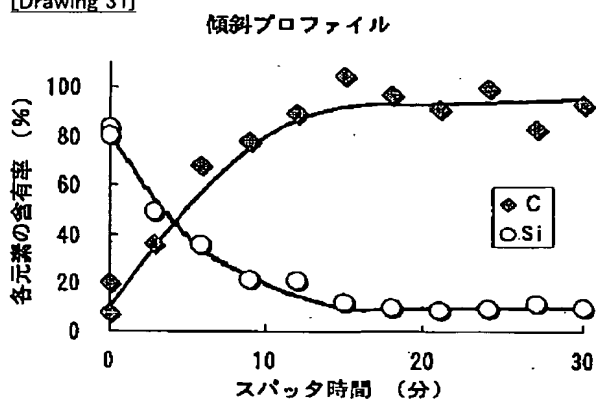
[Drawing 29]



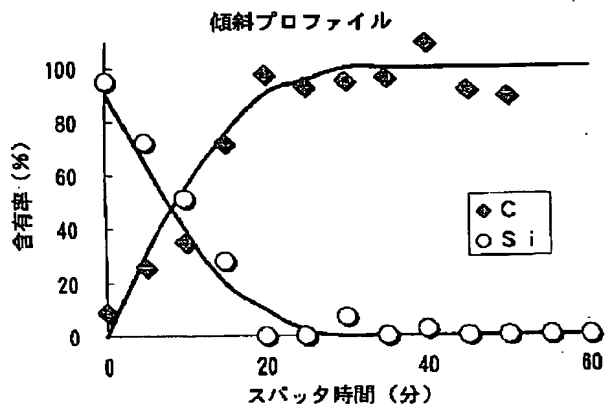
[Drawing 30]



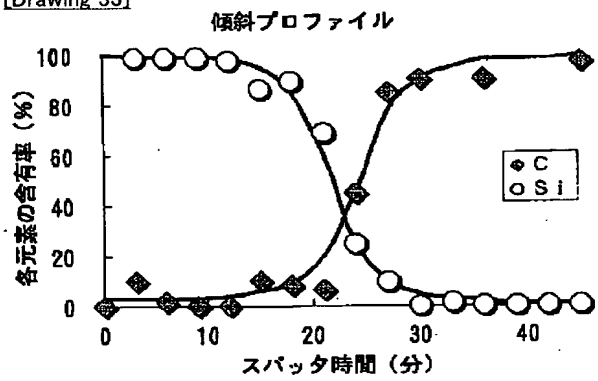
[Drawing 31]



[Drawing 32]



[Drawing 33]



[Translation done.]

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C 09 D 201/00		C 09 D 201/00	4 J 038

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(32) 優先日	平成11年3月24日 (1999.3.24)		
(33) 優先権主張国	日本 (J P)		

最終頁に続く

(54) 【発明の名称】 有機-無機複合傾斜材料、その製造方法及びその用途

(57) 【要約】

【課題】 新規な機能性材料として種々の用途に有用な、厚さ方向に組成が連続的に変化する有機-無機複合傾斜材料、その製造方法および用途を提供する。

【解決手段】 有機高分子化合物と金属系化合物が化学結合した複合体を含有し、該金属系化合物の含有率が、材料表面から深さ方向に連続的に変化する成分傾斜構造を有する有機-無機複合傾斜材料、有機基板上に、特定の有機-無機複合膜形成用塗布液からなる塗膜を形成し、加熱乾燥して上記有機-無機複合傾斜材料を製造する方法、該有機-無機複合傾斜材料からなる被膜形成用コーティング剤および該コーティング剤が塗布された物品である。

【特許請求の範囲】

【請求項1】 有機高分子化合物と金属系化合物との化学結合物を含有する有機-無機複合材料であって、材料中の金属系化合物の含有率が、材料の表面から深さ方向に連続的に変化する成分傾斜構造を有することを特徴とする有機-無機複合傾斜材料。

【請求項2】 有機-無機複合材料が、有機高分子化合物と金属系化合物との化学結合物からなるものである請求項1に記載の有機-無機複合傾斜材料。

【請求項3】 金属系化合物が金属酸化物系化合物である請求項1または2に記載の有機-無機複合傾斜材料。

【請求項4】 金属系化合物が、金属酸化物系化合物を介して有機高分子化合物に化学結合してなる金属窒化物系化合物である請求項1または2に記載の有機-無機複合傾斜材料。

【請求項5】 厚みが5 μ m以下である請求項1～4のいずれか1項に記載の有機-無機複合傾斜材料。

【請求項6】 有機高分子化合物と金属系化合物との化学結合物が、分子中に加水分解により金属酸化物と結合しうる金属含有基を有する有機高分子化合物と、加水分解により金属酸化物を形成しうる金属化合物との混合物を加水分解処理してなるものである請求項3または5に記載の有機-無機複合傾斜材料。

【請求項7】 有機高分子化合物と金属系化合物との化学結合物が、分子中に加水分解により金属窒化物重合体と結合しうる金属含有基を有する有機高分子化合物と、金属窒化物重合体との混合物を加水分解処理してなる請求項4または5に記載の有機-無機複合傾斜材料。

【請求項8】 分子中に加水分解により金属酸化物または金属窒化物重合体と結合しうる金属含有基を有する有機高分子化合物が、上記金属含有基を有する単量体と金属を含まない単量体とを共重合又は縮重合させて得られたものである請求項6または7に記載の有機-無機複合傾斜材料。

【請求項9】 分子中に加水分解により金属酸化物または金属窒化物重合体と結合しうる金属含有基を有する有機高分子化合物が、エチレン性不飽和基を有する単量体と、エチレン性不飽和基および上記金属含有基を含む単量体との共重合体である請求項8に記載の有機-無機複合傾斜材料。

【請求項10】 加水分解により金属酸化物を形成しうる金属化合物が金属アルコキシドである請求項6に記載の有機-無機複合傾斜材料。

【請求項11】 有機基材上に形成された膜状物からなり、かつ実質上、該膜状物の有機基材に当接している面が有機高分子系化合物成分であって、もう一方の開放系面が金属系化合物成分である請求項1～10のいずれか1項に記載の有機-無機複合傾斜材料。

【請求項12】 (A) 分子中に加水分解により金属酸化物または金属窒化物重合体と結合しうる金属含有基を

有する有機高分子化合物と(B)(イ)加水分解により金属酸化物を形成しうる金属化合物、または(ロ)金属窒化物重合体との混合物を加水分解処理せずにまたは加水分解処理して塗布液を調製したのち、有機材からなる基板上に上記塗布液からなる塗膜を形成し、次いで加熱乾燥処理することを特徴とする請求項1～4のいずれか1項に記載の有機-無機複合傾斜材料の製造方法。

【請求項13】 乾燥塗膜の厚みが5 μ m以下である請求項12に記載の方法。

【請求項14】 (A) 成分の分子中に加水分解により金属酸化物または金属窒化物重合体と結合しうる金属含有基を有する有機高分子化合物が、上記金属含有基を有する単量体と金属を含まない単量体とを共重合又は縮重合させて得られたものである請求項12または13に記載の方法。

【請求項15】 (A) 成分の分子中に加水分解により金属酸化物または金属窒化物重合体と結合しうる金属含有基を有する有機高分子化合物が、エチレン性不飽和基を有する単量体と、エチレン性不飽和基および上記金属含有基を含む単量体との共重合体である請求項12～14のいずれか1項に記載の方法。

【請求項16】 (B)(イ) 成分の加水分解により金属酸化物を形成しうる金属化合物が、金属のアルコキシドである請求項12～15のいずれか1項に記載の方法。

【請求項17】 請求項1ないし11のいずれか1項に記載の有機-無機複合傾斜材料からなる被膜を基材上に形成させることを特徴とするコーティング剤。

【請求項18】 (A) 分子中に加水分解により金属酸化物または金属窒化物重合体と結合しうる金属含有基を有する有機高分子化合物と(B)(イ)加水分解により金属酸化物を形成しうる金属化合物、または(ロ)金属窒化物重合体との混合物を加水分解処理せずにまたは加水分解処理して得られた塗布液からなる請求項17に記載のコーティング剤。

【請求項19】 有機基材に対する塗膜形成用として用いられる請求項17または18に記載のコーティング剤。

【請求項20】 有機材料と無機または金属材料との接着剤として用いられる請求項17または18に記載のコーティング剤。

【請求項21】 有機基材と、少なくとも無機系または金属系材料を含むコート層との間に介在させる中間膜形成用として用いられる請求項17または18に記載のコーティング剤。

【請求項22】 少なくとも無機系または金属系材料を含むコート層が光触媒活性材料層である請求項21に記載のコーティング剤。

【請求項23】 少なくとも無機系または金属系材料を含むコート層が無機系または金属系導電性材料層である

請求項21に記載のコーティング剤。

【請求項24】 少なくとも無機系または金属系材料を含むコート層が無機系または金属系材料を含むハードコート層である請求項21に記載のコーティング剤。

【請求項25】 少なくとも無機系または金属系材料を含むコート層が無機系または金属系光記録材料層または無機系または金属系誘電体層である請求項21に記載のコーティング剤。

【請求項26】 表面に有機系塗膜を有する金属系基材と光触媒活性材料層との間に介在させる中間膜形成用として用いられる請求項17または18に記載のコーティング剤。

【請求項27】 光触媒活性材料層が二酸化チタンコーティング膜である請求項22または26に記載のコーティング剤。

【請求項28】 請求項1ないし11のいずれか1項に記載の有機-無機複合傾斜材料を用いたことを特徴とする基材。

【請求項29】 有機基材である請求項28に記載の基材。

【請求項30】 有機基材が、有機-無機複合傾斜材料を中間膜として介在させ、かつ少なくとも無機系または金属系材料を含むコート層を有するものである請求項29に記載の基材。

【請求項31】 有機-無機複合傾斜材料を中間膜として介在させ、かつ光触媒活性材料層を有する、表面に有機系塗膜が設けられる金属系基材である請求項28に記載の基材。

【請求項32】 請求項1ないし11のいずれか1項に記載の有機-無機複合傾斜材料を接着剤として用いたことを特徴とする有機-無機接着材料。

【請求項33】 請求項1ないし11のいずれか1項に記載の有機-無機複合傾斜材料を中間膜として介在させ、かつ少なくとも無機系または金属系材料を含むコート層を有することを特徴とする物品。

【請求項34】 少なくとも無機系または金属系材料を含むコート層が光触媒活性材料層である請求項33に記載の物品。

【請求項35】 少なくとも無機系または金属系材料を含むコート層が無機系または金属系導電性材料層である請求項33に記載の物品。

【請求項36】 少なくとも無機系または金属系材料を含むコート層が無機系または金属系材料を含むハードコート層である請求項33に記載の物品。

【請求項37】 少なくとも無機系または金属系材料を含むコート層が無機系または金属系光記録材料層または無機系または金属系誘電体層である請求項33に記載の物品。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、新規な有機-無機複合傾斜材料、その製造方法および該傾斜材料の用途に関する。さらに詳しくは、本発明は、有機高分子化合物と金属系化合物との化学結合物を含有する有機-無機複合材料であって、該金属系化合物の含有率が材料の厚み方向に連続的に変化する成分傾斜構造を有し、機能性材料として各種用途に有用な有機-無機複合傾斜材料、このものを効率よく製造する方法並びに該傾斜材料からなる被膜形成用コーティング剤、例えば塗膜、有機材料と無機または金属材料との接着剤および有機基材と無機系または金属系材料層との間に介在させる中間膜用などとして用いられるコーティング剤および該傾斜材料を使用した基材や物品に関するものである。

【0002】

【従来の技術】近年、有機高分子材料の性能、機能に関する要求の多様化に伴い、単一の高分子化合物では満足させることが困難となり、高分子化合物に異なる性質をもつ異種材料を加え、複合化することが行われている。例えば、強化材を有機高分子材料中に分散させることによる物性改質が広く行われており、具体的には、炭素繊維、ガラス繊維、金属繊維、セラミックス繊維、アラミド繊維などの有機や無機の繊維状物質、あるいは炭酸カルシウム、シリカ、アルミナなどの粉末状の無機フィラーなどを添加し、均質に分散させることが行われている。また、異種の高分子化合物を混合し、場合により相溶化剤を介して相溶化させ、ポリマーアロイ化することにより、新しい機能を発現させる研究も盛んに行われている。

【0003】一方、最近、材料の組成を少しずつ変化させ、表と裏で性質が全く異なる複合材料である傾斜機能材料が注目され、例えばセラミックスの耐熱性と金属の強度を併せもつ金属-セラミックス複合傾斜機能材料が超音速航空機の機体材料などとして開発されている。

【0004】このような傾斜機能材料は、無機傾斜材料、有機傾斜材料および有機-無機複合傾斜材料に分類され、そして、複数の材料、例えば複数の異種の無機材料同士、複数の異種の有機材料同士、あるいは1種以上の有機材料と1種以上の無機材料を混合し、場所によって異なる分布密度、配向などを制御することで、複数の成分材料の物性を発現させることから、例えば宇宙・航空分野、自動車分野、エレクトロニクス分野、医療分野、エネルギー分野、さらには放射線や電磁波のシールド分野などにおける利用が期待される。

【0005】ところで二酸化チタンなどの半導体を光電極とすることにより、水が水素と酸素とに光分解される、いわゆる本多-藤嶋効果[「工業化学雑誌」第72巻、第108～113ページ(1969年)]が見出されて以来、光触媒の開発や実用化研究が盛んに行われるようになってきた。この光触媒は、例えば、二酸化チタンなどの半導体粒子を、そのバンドギャップ以上のエネ

ルギーの光で励起すると、伝導帯に電子が生じ、かつ価電子帯に正孔が生じ、このエネルギーに富んで電子-正孔対を利用するものである。

【0006】このような光触媒を応用して、例えば脱臭、防汚、抗菌、殺菌、さらには廃水中や廃ガス中の環境汚染上の問題となっている各種物質の分解・除去などが検討されている。光触媒としては、これまで種々の半導体的特性を有する化合物、例えば二酸化チタン、酸化鉄、酸化タングステン、酸化亜鉛などの金属酸化物、硫化カドミウムや硫化亜鉛などの金属硫化物などが知られているが、これらの中で、二酸化チタン、特にアナターゼ型二酸化チタンは実用的な光触媒として有用である。この二酸化チタンは、太陽光などの日常光に含まれる紫外線領域の特定波長の光を吸収することによって優れた光触媒活性を示し、この光触媒作用に由来する強力な酸化作用によって防汚、防臭、抗菌、空気浄化、水浄化、超親水性などの機能を発揮する。

【0007】二酸化チタンなどの光触媒がもつこのような光触媒機能を効果的に発揮させ、それを工業的に利用する研究が現在盛んに行われている。例えば、光触媒を材料の表面に被覆したり、材料表面の塗膜中に混入させておけば、光を照射するだけで材料表面に有機物を分解する作用をもたせることが可能であり、汚れにくいガラスやタイル、便器などで実用化され始めている。また、この光触媒を利用した種々の機能性製品の開発研究が積極的に行われている。例えば(1)大気汚染の元凶となる窒素酸化物を太陽の光エネルギーで分解する建材、(2)透明な光触媒でガラス表面を被覆してなる、付着した汚れを自然分解するとともに、抗菌効果を有するガラス、(3)光触媒の超親水性や防汚性能を利用してフィルム表面に光触媒層を設けてなる、ガラス窓などの表側表面に貼付するウインドフィルム、(4)シリカゲル粒子に二酸化チタン微粉末を被覆してなる排水処理用剤などの実用化が検討されている。

【0008】ところが、光触媒機能をもつ二酸化チタン等の光触媒は、プラスチックなどの有機基板には簡単に担持されず、何らかのバインダーを必要とすることが多い。また該光触媒を有機基板上に直接コーティングしたり、該基材中に混入させると、光触媒作用により有機基板が短時間で劣化するのを免れないと言う問題が生じる。

【0009】このような問題を解決するために、例えば有機基板上に有機系接着剤等を介して二酸化チタン等の光触媒のコーティング膜を設けることも試みられているが、この場合経時的にバインダーと光触媒体との接着性が低下したり、白濁化・干渉色の発生等の好ましくない事態を招来する。また、例えば有機基板上に無機系接着剤等を介して二酸化チタン等の光触媒のコーティング膜を設けることも試みられているが、この場合では、基板との接着性が十分ではなかったり、次第に接着層自体に

クラックなどが発生し、結果として経時的なバインダーと基板との接着性の低下、白濁化・干渉色の発生等の好ましくない事態を招来する。また、二酸化チタン等の光触媒をシリカで被覆したマイクロカプセルが開発され、このマイクロカプセルを有機基体中に混入して、消臭・抗菌機能を付与することが試みられている。このようなマイクロカプセルは、光触媒が表面に露出し難いため、有機基板の劣化が抑制されるとともに、カプセルには微小な孔が多数存在しており、分子の小さな有機物は入り込むことが出来るので、触媒機能は効果的に発揮される。しかしながら、このような構造のマイクロカプセルは、その光触媒活性を高活性にすることも難しく、また光触媒のもう一つの特徴である親水化現象を十分に応用することは困難である。またその製造方法に煩雑な操作を必要とし、製造コストが高つくのを免れないという欠点を有している。

【0010】他方、プラスチック基材上に、前記光触媒活性材料以外の様々な無機系または金属系材料、例えば導電性材料、ハードコート剤、光記録材料、磁性粉、赤外線吸収材料などからなる層を設け、機能性材料を作製することが広く行われている。プラスチック基材上に、このような無機系または金属系材料層を設ける場合、一般に基材との密着性が不十分であるために、例えばプラスチック基材上に無機系プライマー層を設け、その上に無機系または金属系材料層を形成させる方法が、よく用いられる。しかしながら、この方法においては、無機系プライマー層と無機系または金属系材料層との密着性は良好であるものの、プラスチック基材と無機系プライマー層との密着性は必ずしも十分ではなく、耐熱密着性に劣ったり、あるいは経時により密着性が低下したりするなどの問題があった。したがって、プラスチック基材上に無機系または金属系材料層を密着性よく形成させる技術の開発が望まれていた。

【0011】

【発明が解決しようとする課題】本発明は、このような事情のもとで、新規な機能性材料として種々の用途、例えば塗膜や、有機材料と無機または金属材料との接着剤、有機基材と光触媒塗膜との間に設けられ、有機基材の劣化を防止する中間膜や、有機基材と無機系または金属系材料層との密着性を向上させる中間膜などの用途に有用な、厚さ方向に組成が連続的に変化する有機-無機複合傾斜材料、このものを効率よく製造する方法およびその用途を提供することを目的とするものである。

【0012】

【課題を解決するための手段】本発明者らは、前記目的を達成するために鋭意研究を重ねた結果、分子中に加水分解により金属酸化物または金属窒化物重合体と結合しうる金属含有基を有する有機高分子化合物と加水分解により金属酸化物を形成しうる金属化合物、または金属窒化物重合体との混合物を加水分解処理せずまたは加水

分解処理して得られた塗布液を有機基板上に塗布し、加熱乾燥処理することにより形成される有機高分子化合物と金属系化合物との化学結合物を含有する有機-無機複合材料が、材料中の金属系化合物の含有率が材料の表面から深さ方向に連続的に変化する成分傾斜構造を有する新規な有機-無機複合傾斜材料であり、前記用途に有用であることを見出し、この知見に基づいて本発明を完成するに至った。

【0013】すなわち、本発明は、(1)有機高分子化合物と金属系化合物との化学結合物を含有する有機-無機複合材料であって、材料中の金属系化合物の含有率が、材料の表面から深さ方向に連続的に変化する成分傾斜構造を有することを特徴とする有機-無機複合傾斜材料、(2)上記有機-無機複合傾斜材料からなる被膜を基材上に形成させることを特徴とするコーティング剤、好ましくは有機基材に対する塗膜形成用、有機材料と無機または金属材料との接着剤用および有機基材と少なくとも無機系または金属系材料を含むコート層との間に介在させる中間膜形成用として用いられるコーティング剤、(3)上記有機-無機複合傾斜材料を用いたことを特徴とする基材、(4)上記有機-無機複合傾斜材料を接着剤として用いたことを特徴とする有機-無機接着材料、および(5)上記有機-無機複合傾斜材料を中間膜として介在させ、かつ少なくとも無機系または金属系材料を含むコート層を有することを特徴とする物品、を提供するものである。

【0014】また、前記有機-無機複合傾斜材料は、本発明に従えば、(A)分子中に加水分解により金属酸化物または金属窒化物重合体と結合しうる金属含有基を有する有機高分子化合物と(B)(イ)加水分解により金属酸化物を形成しうる金属化合物、または(ロ)金属窒化物重合体との混合物を加水分解処理せずにまたは加水分解処理して塗布液を調製したのち、有機材からなる基板上に上記塗布液からなる塗膜を形成し、次いで加熱乾燥処理することにより製造することができる。

【0015】

【発明の実施の形態】本発明の有機-無機複合傾斜材料は、有機高分子化合物と金属系化合物とが化学結合してなる複合体を含有する有機-無機複合材料、好ましくは該複合体からなる有機-無機複合材料であって、材料中の金属系化合物の含有率が、材料表面から深さ方向に連続的に変化する成分傾斜構造を有するものである。

【0016】このような成分傾斜構造の確認は、例えば、有機材からなる基板上に設けた有機-無機複合傾斜材料の塗膜表面に、スパッタリングを施して膜を削っていき、経時的に膜表面の炭素原子と金属原子の含有率を、X線光電子分光法などにより測定することによって、行うことができる。具体的に例を挙げて説明すると、図1は、後述の実施例1において、ポリメチルメタクリレート基板上に設けられた厚さ0.6μmの有機-

無機複合材料(金属原子として、ケイ素原子を含む)からなる塗膜における、スパッタリング時間と炭素原子及びケイ素原子の含有率との関係を示すグラフであって、この図から分かるように、スパッタリングを施す前の塗膜表面は、ほぼ100%近くケイ素原子で占められているが、スパッタリングにより膜が削られていくに伴い、膜表面のケイ素原子の含有率が減少するとともに、炭素原子の含有率が増加し、スパッタリング時間が約30分間を過ぎた時点から、膜表面はほぼ炭素原子のみとなる。

【0017】すなわち、この傾斜材料においては、材料中の金属酸化物系化合物の含有率が、表面から基板方向に逐次減少していることが示されている。

【0018】本発明の有機-無機複合傾斜材料は、有機高分子化合物に金属系化合物が化学結合した複合体を含有することを特徴としており、このような化学結合による複合体は、後で説明する本発明の方法によって容易に形成させることができる。

【0019】本発明の傾斜材料における金属系化合物の種類については特に制限はなく、金属酸化物系化合物、または金属酸化物系化合物を介して有機高分子化合物に化学結合してなる金属窒化物系化合物などを挙げることができるが、ゾル-ゲル法により形成されうるものが好ましく、このような金属系化合物としては、例えばケイ素、チタン、ジルコニウム及びアルミニウムの中から選ばれる金属の酸化物系化合物を好ましく挙げることができる。これらの金属系化合物は1種の金属を含むものであってもよいし、2種以上の金属を含むものであってもよい。

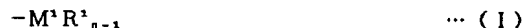
【0020】また本発明の傾斜材料における上記金属系化合物の含有量としては特に制限はないが、金属酸化物換算で、通常5~98重量%、好ましくは20~98重量%、特に好ましくは50~90重量%の範囲である。有機高分子化合物の重合度や分子量としては、製膜化しうるものであればよく特に制限されず、高分子化合物の種類や所望の塗膜物性などに応じて適宜選定すればよい。さらに、本発明の傾斜材料は、その厚みが5μm以下、特に0.01~1.0μmの範囲のものが、傾斜性及び塗膜性能などの点から好適である。

【0021】このような有機-無機複合傾斜材料は、以下に示す本発明の方法により効率よく製造することができる。本発明の方法においては、まず(A)分子中に加水分解により金属酸化物または金属窒化物重合体と結合しうる金属含有基(以下、加水分解性金属含有基と称することがある。)を有する有機高分子化合物と(B)(イ)加水分解により金属酸化物を形成しうる金属化合物(以下、加水分解性金属化合物と称することがある。)、または(ロ)金属窒化物重合体との混合物を加水分解処理せずにまたは加水分解処理して塗布液を調製する。

【0022】上記(A)成分である有機高分子化合物中の加水分解により金属酸化物または金属窒化物重合体と結合しうる金属含有基及び(B)(イ)成分である加水分解により金属酸化物を形成しうる金属化合物、または(ロ)成分の金属窒化物重合体における金属としては、例えばケイ素、チタン、ジルコニウム及びアルミニウムの中から選ばれる少なくとも1種を好ましく挙げることができる。

【0023】上記(A)成分である分子中に加水分解により金属酸化物または金属窒化物重合体と結合しうる金属含有基を有する有機高分子化合物は、例えば該金属含有基を有する単量体と金属を含まない単量体とを共重合又は縮重合させることにより、得ることができる。

【0024】ここで加水分解により金属酸化物または金属窒化物重合体と結合しうる金属含有基としては、例えば一般式(I)

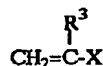


(式中、 R^1 は加水分解性基または非加水分解性基であるが、その中の少なくとも1つは加水分解により、

(B)成分と化学結合しうる加水分解性基であることが必要であり、また、 R^1 が複数の場合には、各 R^1 はたがいに同一であってもよいし、異なってもよく、 M^1 はケイ素、チタン、ジルコニウム、アルミニウムなどの金属原子、 n は金属原子 M^1 の価数である。)で表される基を挙げることができる。

【0025】上記一般式(I)において、 R^1 のうちの加水分解により(B)成分と化学結合しうる加水分解性基としては、例えばアルコキシ基、イソシアネート基、塩素原子などのハロゲン原子、オキシハロゲン基、アセチルアセトネート基などが挙げられ、一方、(B)成分と化学結合しない非加水分解性基としては、例えば低級アルキル基などが好ましく挙げられる。

【0026】上記一般式(I)で表される金属含有基としては、例えば、トリメトキシシリル基、トリエトキシシリル基、トリ-n-プロポキシシリル基、トリイソプロポキシシリル基、トリ-n-ブトキシシリル基、トリイソブトキシシリル基、トリ-sec-ブトキシシリル基、トリ-tert-ブトキシシリル基、トリクロロシリル*



(式中、 R^3 は水素原子またはメチル基、 X は一価の有機基である。)で表されるエチレン性不飽和基を有する単量体、特に好ましくは一般式(III-a)

【化3】



(式中、 R^4 はアルキル基、シクロアルキル基、アリー

*基、ジメチルメトキシシリル基、メチルジメトキシシリル基、ジメチルクロロシリル基、メチルジクロロシリル基、トリイソシアナトシリル基、メチルジイソシアナトシリル基など、トリメトキシチタニウム基、トリエトキシチタニウム基、トリ-n-プロポキシチタニウム基、トリイソプロポキシチタニウム基、トリ-n-ブトキシチタニウム基、トリイソブトキシチタニウム基、トリ-sec-ブトキシチタニウム基、トリ-tert-ブトキシチタニウム基、トリクロロチタニウム基、さらには、トリメトキシジルコニウム基、トリエトキシジルコニウム基、トリ-n-プロポキシジルコニウム基、トリイソプロポキシジルコニウム基、トリ-n-ブトキシジルコニウム基、トリイソブトキシジルコニウム基、トリ-sec-ブトキシジルコニウム基、トリ-tert-ブトキシジルコニウム基、トリクロロジルコニウム基、またさらには、ジメトキシアルミニウム基、ジエトキシアルミニウム基、ジ-n-プロポキシアルミニウム基、ジイソプロポキシアルミニウム基、ジ-n-ブトキシアルミニウム基、ジイソブトキシアルミニウム基、ジ-sec-ブトキシアルミニウム基、ジ-tert-ブトキシアルミニウム基、トリクロロアルミニウム基などが挙げられる。

【0027】上記共重合の例としては、エチレン性不飽和基および前記一般式(I)で表される金属含有基を有する単量体と、エチレン性不飽和基を有し、かつ金属を含まない単量体とをラジカル共重合させることにより、所望の高分子化合物が得られる。具体的には、一般式(II)

【化1】



(式中、 R^2 は水素原子またはメチル基、 A はアルキレン基、好ましくは炭素数1~4のアルキレン基、 R^1 、 M^1 および n は前記と同じである。)で表される金属含有基を含むアルキル基をエステル成分とする(メタ)アクリル酸エステル1種以上と、一般式(III)

【化2】

...(III)

ル基またはアラルキル基であり、 R^1 は前記と同じである。)で表される(メタ)アクリル酸エステル1種以上とをラジカル共重合させる方法を挙げることができる。

【0028】一方、縮重合の例としては、上記エチレン性不飽和基の代わりに、縮合により高分子量化可能な基、例えば縮合によりアミド結合、エステル結合あるいはウレタン結合などを生成する2つ以上の官能基と前記一般式(I)で表される金属含有基とを有する単量体

と、縮合により高分子量化可能な基、例えば縮合によりアミド結合、エステル結合あるいはウレタン結合などを生成する2つ以上の官能基を有し、かつ金属含有基を含まない単量体とを縮重合させる方法などにより、所望の高分子化合物が得られる。

【0029】具体的には、いずれか一方の成分が前記一般式(I)で表される金属含有基を有するアミン成分と酸成分とを縮重合させ、ポリアミドを形成させる方法、あるいはいずれか一方の成分が前記一般式(I)で表される金属含有基を有するアルコール成分と酸成分とを縮重合させ、ポリエステルを形成させる方法などが挙げられる。

【0030】上記(B)(イ)成分である加水分解により金属酸化物を形成しうる金属化合物(加水分解性金属化合物)としては、例えば一般式(IV)

$M^m R^1$... (IV)

(式中、 R^1 は加水分解性基または非加水分解性基であるが、少なくとも2つは加水分解性基であり、かつ少なくとも1つは、加水分解により(A)成分と化学結合しうる加水分解性基であって、複数の R^1 はたがいに同一であってよいし、異なっていてよく、 M^1 はケイ素、チタン、ジルコニウム、アルミニウムなどの金属原子、 m は金属原子 M^1 の価数である。)で表される金属化合物を挙げることができる。

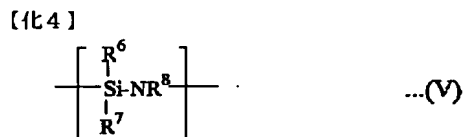
【0031】上記一般式(IV)における R^1 のうちの加水分解性基としては、例えばアルコキシ基、イソシアネート基、塩素原子などのハロゲン原子、オキシハロゲン基、アセチルアセトネート基などが挙げられ、一方非加水分解性基としては、例えば低級アルキル基、アリール基、アルケニル基などが好ましく挙げられる。この加水分解性金属化合物としては、上記一般式(IV)で表される金属化合物から誘導されるオリゴマーや、一般式(IV)で表される金属化合物を複数種混合したものを用いることができる。

【0032】上記一般式(IV)で表される金属化合物の例としては、テトラメトキシシラン、テトラエトキシシラン、テトラ- n -プロポキシシラン、テトライソプロポキシシラン、テトラ- n -ブトキシシラン、テトライソブトキシシラン、テトラ- sec -ブトキシシラン、テトラ- $tert$ -ブトキシシランなど、並びにこれらに対応するテトラアルコキシチタンおよびテトラアルコキシジルコニウム、さらにはトリメトキシアルミニウム、トリエトキシアルミニウム、トリ- n -プロポキシアルミニウム、トリイソプロポキシアルミニウム、トリ- n -ブトキシアルミニウム、トリイソブトキシアルミニウム、トリ- sec -ブトキシアルミニウム、トリ- $tert$ -ブトキシアルミニウムなどの金属アルコキシド、あるいは金属アルコキシドオリゴマー、例えば市販品のアルコキシシランオリゴマーである「メチルシリケート51」、「エチルシリケート40」(いずれもコルコート社製商

品名)など、さらにはテトライソシアナトシラン、メチルトリイソシアナトシラン、テトラクロロシラン、メチルトリクロロシランなどが挙げられるが、この(B)

(イ)成分としては、金属のアルコキシドが好適である。これらは単独で用いてもよいし、2種以上を組み合わせ用いてもよい。

【0033】一方(B)(ロ)成分である金属窒化物重合体としては、例えば一般式(V)



(式中、 R^6 、 R^7 および R^8 は、それぞれ独立に水素原子、アルキル基、アルケニル基、アリール基、アラルキル基、若しくはこれらの基以外のフルオロアルキル基などの炭素原子がケイ素原子に直結する基、アルキルシリル基、アルキルアミノ基またはアルコキシ基であるが、その少なくとも1つは水素原子である。)で表される構造単位を含む数平均分子量100~50000のポリシラザンなどを好ましく挙げることができる。

【0034】本発明の方法においては、(B)(イ)成分として金属アルコキシドを用いる場合にはアルコール、ケトン、エーテルなどの適当な極性溶剤中において、前記(A)成分の高分子化合物および(B)(イ)成分の金属アルコキシドの混合物を、塩酸、硫酸、硝酸などの酸、あるいは固体酸としてのカチオン交換樹脂を用い、通常0~60℃、好ましくは20~40℃の温度にて加水分解処理し、固体酸を用いた場合には、それを除去したのち、さらに、所望により溶剤を留去または添加し、塗布するのに適した粘度に調整して塗布液を調製する。温度が低すぎる場合は加水分解が進まず、高すぎる場合は逆に加水分解が進みすぎ、その結果得られる傾斜塗膜の傾斜性が低下するおそれがある。なお、(B)(イ)成分の金属アルコキシドを含む極性溶剤溶液を予め調製し、これに酸を加えて加水分解反応を進めておき、このものと(A)成分を混合し、さらに加水分解処理してもよい。

【0035】また、(B)(イ)成分として、イソシアネート系金属化合物やハロゲン系金属化合物を用いる場合、あるいは(B)(ロ)成分を用いる場合には、通常成膜前には加水分解処理は行わず、成膜時またはそれ以降において、空気中の水分により加水分解させる方法が用いられる。

【0036】無機成分は、その種類によっては塗布液調製後も、加水分解、重縮合が徐々に進行して塗布条件が変動する場合があるので、塗布液に不溶の固体の脱水剤、例えば無水硫酸マグネシウムなどを添加することにより、ポットライフの低下を防止することができる。こ

の場合、塗布液は、該脱水剤を除去してから、塗布に用いる。

【0037】次に、このようにして得られた塗布液を用い、有機材からなる基板に、乾燥塗膜の厚さ、通常5 μm 以下、特に中間膜用途として、好ましくは0.01~1.0 μm 、より好ましくは0.02~0.7 μm の範囲になるように、ディップコート法、スピンコート法、スプレーコート法、バーコート法、ナイフコート法、ロールコート法、ブレードコート法、ダイコート法、グラビアコート法などの公知の手段により塗膜を形成し、公知の乾燥処理、例えば40~150℃程度の温度で加熱乾燥処理することにより、本発明の有機-無機複合傾斜材料が得られる。

【0038】本発明においては、(A)成分と(B)

(イ)成分のうちの金属アルコキシドとの混合物の加水分解処理により、(A)成分の高分子化合物中の加水分解性金属含有基が加水分解するとともに、(B)(イ)成分の金属アルコキシドも加水分解して一部重合する。次に、この塗布液を有機材からなる基板(有機基材と称することがある。)に塗布することにより、(A)成分の高分子化合物中のフレキシブルな高分子鎖の部分が基板に吸着されるとともに、側鎖の金属含有基の加水分解部分は基板から離れたところに位置する。この塗膜を加熱乾燥処理することにより、上記側鎖の金属含有基の加水分解がさらに進行するとともに、(B)(イ)成分の金属アルコキシドの加水分解、重合もさらに進行し、そしてこの際、上記側鎖の加水分解により生成した反応性基、例えばシラノール基と(B)(イ)成分の加水分解、重合物とが縮合(化学結合)することにより、高分子化合物と金属酸化物系化合物とが化学結合した複合体が形成する。

【0039】また、(A)成分と(B)(イ)成分のうちのイソシアネート系やハロゲン系金属化合物または(B)(ロ)成分との混合物からなる塗布液を有機材からなる基板に塗布することにより、(A)成分の高分子化合物中のフレキシブルな高分子鎖の部分が基板に吸着されるとともに、側鎖の加水分解性金属含有基は基板から離れたところに位置する。この塗膜は成膜時または加熱乾燥処理時に空気中の水分により、上記側鎖の加水分解性金属含有基の加水分解が進行するとともに、上記側鎖の加水分解により生成した反応性基、例えばシラノール基と(B)(イ)成分のイソシアネート系やハロゲン系金属化合物の加水分解物または(B)(ロ)成分の金属窒化物重合物とが化学結合した複合体が形成する。したがって、本発明の複合傾斜材料は、特開平8-283425号公報に記載されている傾斜複合体とは根本的に異なるものである。

【0040】このようにして有機基材上に形成された本発明の複合傾斜材料においては、材料中の金属系化合物の含有率は、表面ではほぼ100%であるが、基板方向

に逐次減少していき、基板近くでは、ほぼ0%になる。すなわち、本発明の複合傾斜材料は、一般に、有機基材上に形成された膜状物からなり、かつ実質上、該膜状物の有機基材に当接している面が有機高分子系化合物成分であって、もう一方の開放系面が金属系化合物である。

【0041】本発明においては、前記機構により複合傾斜材料が形成されることから、塗膜の形成後、有機材からなる基板に高分子鎖の部分が吸着されるのに必要な時間、一般的には少なくとも液体状態を数秒間程度保持することが肝要である。使用する有機成分の可溶性溶媒と無機成分の可溶性溶媒は、通常は異なる溶媒が用いられ、それらが混和性を有する必要がある。また、塗工機あるいはスプレー法等での塗布において、厚み斑がなくかつ良好な傾斜構造を得るためには、無機成分同士が縮合する前に高分子化合物の吸着が起こるようにするためにも、上記無機成分可溶性溶媒の蒸発点を有機成分可溶性溶媒の蒸発点以上に高くするのが好ましい。なお、有機成分と無機成分の両者を溶解できるものであれば、単独溶媒でも使用可能である。

【0042】有機材からなる基板としては特に制限はなく、例えばポリメチルメタクリレートなどのアクリル樹脂、ポリスチレンやABS樹脂などのスチレン系樹脂、ポリエチレンやポリプロピレンなどのオレフィン系樹脂、ポリエチレンテレフタレートやポリエチレンナフタレートなどのポリエステル系樹脂、6-ナイロンや6,6-ナイロンなどのポリアミド系樹脂、ポリ塩化ビニル系樹脂、ポリカーボネート系樹脂、ポリフェニレンサルファイド系樹脂、ポリフェニレンエーテル系樹脂、ポリイミド系樹脂、セルロースアセテートなどのセルロース系樹脂などからなる基板を挙げることができる。

【0043】これらの基板は、本発明の傾斜材料との密着性をさらに向上させるために、所望により、酸化法や凹凸化法などにより表面処理を施すことができる。上記酸化法としては、例えばコロナ放電処理、クロム酸処理(湿式)、火炎処理、熱風処理、オゾン・紫外線照射処理などが挙げられ、また、凹凸化法としては、例えばサンドブラスト法、溶剤処理法などが挙げられる。これらの表面処理法は基板の種類に応じて適宜選ばれる。

【0044】なお、本発明における有機材からなる基板は、有機系材料以外の材料、例えば金属系材料、ガラスやセラミックス系材料、その他各種無機系または金属系材料からなる基材の表面に、有機系塗膜を有するものも包含する。

【0045】このようにして得られた本発明の有機-無機複合傾斜材料は、前記したような優れた傾斜性を有するとともに、(1)基板と無機膜の熱収縮あるいは物理的伸縮に対する応力を緩和する性質、(2)屈折率が連続的に変化する、(3)無機成分や有機成分の混合比によって、任意かつ簡単にその傾斜性を制御しうる、(4)無機成分の形態による成膜時の表面構造の制御が可能である

などの性質を有することから、新しい機能性材料として、種々の用途に有用である。

【0046】本発明はまた、該有機-無機複合傾斜材料からなる被膜を基材上に形成させるコーティング剤をも提供するものである。このコーティング剤としては、前記の(A)分子中に加水分解により金属酸化物または金属窒化物重合体と結合しうる金属含有基を有する有機高分子化合物と(B)(イ)加水分解により金属酸化物を形成しうる金属化合物、または(ロ)金属窒化物重合体との混合物を加水分解処理せずにまたは加水分解処理して得られた塗布液からなるものを好ましく挙げることができる。

【0047】このコーティング膜は下記の用途に用いることができる。まず、塗膜としての用途に用いられる。該有機-無機複合傾斜材料は、有機基材に対する接着性に優れており、かつ塗膜表面は金属酸化物または金属窒化物の性質を有することから、例えば各種プラスチックフィルム上に該材料からなるコート層を設けることにより、耐擦傷性や耐熱性に優れると共に、密着性の良好なハードコートフィルムを得ることができる。

【0048】次に、接着剤としての用途に用いられる。本発明の傾斜材料は、前記したように有機基材との密着性に優れるとともに、表面は金属系化合物であるので、無機または金属材料との密着性に優れている。したがって、有機材料と無機または金属材料との接着剤として好適である。

【0049】さらに、有機基材と、少なくとも無機系または金属系材料を含むコート層との間に介在させる中間膜としての用途に用いられる。有機基材上に無機系または金属系材料を含むコート層を形成する場合、一般に有機基材と該コート層との密着性が不十分であって、耐久性に劣り、経時により剥離したり、あるいは熱や湿気などにより剥離しやすくなるという問題が生じる。

【0050】本発明の傾斜材料を中間膜として、上記有機基材と無機系または金属系材料を含むコート層との間に介在させることにより、該中間膜は前記したように傾斜性を有することから、有機基材との密着性に優れると共に、その上に設けられる無機系または金属系材料を含むコート層との密着性にも優れ、その結果、有機基材上に無機系または金属系材料を含むコート層を極めて密着性よく、形成させることができる。本発明においては、該中間膜の厚さは、通常5 μ m以下、好ましくは0.01~1.0 μ m、より好ましくは0.02~0.7 μ mの範囲である。

【0051】前記無機系または金属系材料を含むコート層としては特に制限はなく、様々なコート層を形成することができるが、例えば(1)光触媒活性材料層、

(2)無機系または金属系導電性材料層、(3)無機系または金属系材料を含むハードコート層、(4)無機系または金属系光記録材料層または無機系または金属系誘

電体層などを好ましく挙げることができる。

【0052】次に、各無機系または金属系材料を含むコート層について説明する。

(1)光触媒活性材料層：有機基材表面に、二酸化チタンなどの光触媒活性材料のコート層を設けた場合、その光触媒作用により、有機基材が短時間で劣化するという問題が生じる。したがって、光触媒作用により、劣化しにくい無機バインダーを介して有機基材上に二酸化チタンなどの光触媒活性材料のコート層を設けることが試みられている。しかしながら、無機バインダーは、有機基材との接着力が不十分であり、耐久性に劣るという問題がある。

【0053】本発明の傾斜材料を中間膜として、有機基材と光触媒活性材料のコート層との間に介在させた場合、有機基材との密着性に優れ、しかも表面はほぼ金属系化合物であるため、光触媒活性材料のコート層との密着性が良い上、中間膜が光触媒作用により劣化しにくく、有機基材を十分に保護することができる。

【0054】また、表面に有機系塗膜を有する金属系基材と光触媒活性材料層との間に、本発明の傾斜材料を中間膜として介在させることができる。この中間膜は、上記有機基材の場合と同様に、有機系塗膜との密着性に優れ、しかも光触媒活性材料のコート層との密着性が良い上、光触媒作用により劣化しにくく、有機系塗膜を十分に保護することができる。このような用途としては、特に表面に有機系塗膜を有する自動車用鋼板上に光触媒活性材料層を設ける場合に有用である。

【0055】表面に有機系塗膜を有する金属系基材としては、例えば冷延鋼板、亜鉛めっき鋼板、アルミニウム/亜鉛合金めっき鋼板、ステンレス鋼板、アルミニウム板、アルミニウム合金板などの金属系基材に有機系塗膜を形成したものを挙げることができる。本発明の傾斜材料を、このような中間膜として用いる場合、その上に設けられる光触媒活性材料のコート層が光触媒能の高い二酸化チタンである場合に、特に有効である。

【0056】(2)無機系または金属系導電性材料層：表面に導電性材料層を有する有機基材、特にプラスチックフィルムは、エレクトロルミネッセンス素子(EL素子)、液晶表示素子(LCD素子)、太陽電池などに用いられ、さらに電磁波遮蔽フィルムや帯電防止性フィルムなどとして用いられている。このような用途に用いられる導電性材料としては、例えば酸化インジウム、酸化錫、酸化亜鉛、酸化カドミウム、ITO(インジウムチンオキシド)などの金属酸化物や、金、白金、銀、ニッケル、アルミニウム、銅のような金属などの無機系または金属系導電性材料が用いられる。そして、これらの無機系または金属系導電性材料は、通常真空蒸着法、スパッタリング法、イオンプレーティング法などの公知の手段により、プラスチックフィルムなどの有機基材上に、厚さ50~2000オングストローム程度の薄膜として

形成される。

【0057】このようにして形成された無機系または金属系導電性材料層は、有機基材との密着性が不十分であるので、本発明の傾斜材料を中間膜として、有機基材と該無機系または金属系導電性材料層との間に介在させることにより、有機基材と無機系または金属系導電性材料層との密着性を向上させることができる。また、透明導電性フィルムが要求される場合においても、本発明の傾斜材料からなる中間膜を介在させることにより、透明性が損なわれることはほとんどない。

【0058】(3) 無機系または金属系材料を含むハードコート層：表面硬度が良好で、優れた耐擦傷性や耐摩耗性を有するハードコートフィルムは、例えば、車両、建物などの窓ガラスや窓用プラスチックボードなどの表面貼付用として、あるいはCRTディスプレイやフラットパネルディスプレイなどの保護用などとして広く用いられている。

【0059】一方、プラスチックレンズは、ガラスレンズに比べて、軽量でかつ安全性、加工性、ファッション性などに優れていることから、近年急速に普及してきている。しかしながら、このプラスチックレンズは、ガラスレンズに比べて傷が付きやすいという欠点を有しており、したがって、その表面をハードコート層で被覆することが行われている。

【0060】このようなハードコートフィルムやプラスチックレンズに設けられるハードコート層の材料としては、例えばアルキルトリヒドロキシシランおよびその部分縮合物とコロイダルシリカとシリコン変性アクリル樹脂とからなる混合物、オルガノトリアルコキシシラン加水分解縮合物、アルコキシシラン加水分解縮合物とコロイダルシリカとの混合物、ジルコニウム、アルミニウムおよびチタニウムの中から選ばれる金属とキレート化合物とシリコン変性アクリル樹脂とからなる混合物などの無機系または金属系材料を含むハードコート剤が多用されている。

【0061】プラスチックフィルムやプラスチックレンズなどの有機基材上にハードコート層を形成するには、前記の無機系または金属系材料を含むハードコート剤を、公知の方法、例えばバーコート法、ナイフコート法、ロールコート法、ブレードコート法、ダイコート法、グラビアコート法、スプレーコート法などを用いて、乾燥膜厚が1~30μm程度になるように有機基材上に塗布し、乾燥処理する方法が、通常用いられる。

【0062】このようにして形成された無機系または金属系材料を含むハードコート層は、有機基材との密着性が不十分であるので、本発明の傾斜材料を中間膜として、有機基材と該ハードコート層との間に介在させることにより、有機基材と無機系または金属系材料を含むハードコート層との密着性を向上させることができる。またプラスチックレンズにおいて、本発明の傾斜材料から

なる中間膜を介在させても、該プラスチックレンズの透明性の低下や干渉縞の発生などをもたらすことはほとんどない。

【0063】(4) 無機系または金属系光記録材料層または無機系または金属系誘電体層：近年、書き換え可能、高密度、大容量の記憶容量、記録再生ヘッドと非接触等という特徴を有する光記録媒体として、半導体レーザー光等の熱エネルギーを用いて磁性膜の磁化反転を利用して情報を記録し磁気光学効果を利用して読み出す光磁気ディスクや結晶から、アモルファスへの相変化を利用した相変化ディスクが開発され、実用化に至っている。

【0064】このような光記録媒体は、一般に、透光性樹脂基板（有機基材）、例えばポリカーボネートやポリメチルメタクリレートなどの基板上に光記録材料層、誘電体層、金属反射層、有機保護層などが順次積層された構造を有しており、また、基板と光記録材料層との間に、誘電体下地層を設ける場合もある。

【0065】基板上に設けられる光記録材料層には、例えばTb-Fe、Tb-Fe-Co、Dy-Fe-Co、Tb-Dy-Fe-Coなどの無機系の光磁気型記録材料、あるいはTeOx、Te-Ge、Sn-Te-Ge、Bi-Te-Ge、Sb-Te-Ge、Pb-Sn-Te、Tl-In-Seなどの無機系の相変化型記録材料が用いられる。また、所望により、基板と光記録材料層との間に設けられる誘電体下地層には、例えばSiN、SiO、SiO₂、Ta₂O₅などの無機系材料が用いられる。前記無機系の光記録材料層や誘電体下地層は、通常真空蒸着法、スパッタリング法、イオンプレーティング法などの公知的手段によって形成される。

【0066】このようにして形成された無機系または金属系光記録材料層または無機系誘電体下地層は、透光性樹脂基板との密着性が不十分であるので、本発明の傾斜材料を中間膜として、透光性樹脂基板と該光記録材料層または該誘電体下地層との間に介在させることにより、基板と光記録材料層または誘電体下地層との密着性を向上させることができる。

【0067】その他無機系または金属系材料を含むコート層としては、酸化チタン、酸化亜鉛、酸化インジウム、酸化錫、硫化亜鉛、アンチモンドープ酸化錫（ATO）、錫ドープ酸化インジウム（ITO）などの無機系赤外線吸収剤層、メタル蒸着された磁性層などが挙げられる。

【0068】本発明は、さらに、上記有機-無機複合傾斜材料を用いてなる基材、該複合傾斜材料を接着剤として用いてなる有機-無機接着材料および該複合傾斜材料を中間膜として介在させ、かつ少なくとも無機系または金属系材料を含むコート層を有する物品をも提供する。

【0069】前記基材の具体例としては、本発明の有機-無機複合傾斜材料を中間膜として介在させ、かつ少な

くとも無機系または金属系材料を含むコート層を有する有機基材、あるいは、本発明の有機-無機複合傾斜材料を中間膜として介在させ、かつ光触媒活性材料層を有する、表面に有機系塗膜が設けられた金属系基材などを好ましく挙げることができる。

【0070】また、物品の具体例としては、少なくとも無機系または金属系材料を含むコート層が、(1)光触媒活性材料層、(2)無機系または金属系導電性材料層、(3)無機系または金属系材料を含むハードコート層、および(4)無機系または金属系光記録材料層または無機系または金属系誘電体層であるものなどを好ましく挙げることができる。

【0071】本発明の有機-無機複合傾斜材料の用途としては、上述の用途以外に、例えば(1)強誘電体薄膜(チタン酸バリウム、チタン酸鉛、チタン酸ストロンチウム等)の中間膜

(2)金属蒸着薄膜からなるUVカットフィルムの中間膜、(3)金属蒸着薄膜からなる熱線遮蔽フィルムの中間膜、(4)シリカーチタニア積層膜からなる低反射・無反射コーティング膜の中間膜、(5)シリカーチタニア積層膜からなるヘッドアップディスプレイコンバイナーフィルムの中間膜、(6)ゾルゲル法により無機酸化物に機能性分子をドーピングさせた薄膜用の中間膜(シリカ等の無機成分中に、蛍光色素、レーザー用色素、フォトクロミック材料、エレクトロクロミック材料、非線形工学材料を分散させた薄膜)、(7)塗布用無機系抗菌材用のアンダーコート、(8)無機成分がシリカからなる傾斜膜表面のOH基を利用してカップリング反応により、酵素、抗体、蛋白質等の分子を化学結合させる固定化用膜としての利用、

【0072】(9)傾斜膜表面のシリカのOH基を利用して、シラン系カップリング剤やチタネート系カップリング剤、アルミネート系カップリング剤、ジルコネート系カップリング剤等の反応サイトとしての利用、(10)傾斜膜表面のシリカのOH基を利用して、重合可能な官能基を結合させ、グラフト反応場としての利用、

(11)プラスチックの耐蝕コーティング(チタニア、アルミナ、ジルコニア及びチタニア-シリカ、アルミナ-シリカ、ジルコニア-シリカ等の複合酸化物)、(12)プラスチックの耐熱コーティング、(13)プラスチック表面のブリードアウト防止コーティング(プラスチック中の添加剤の表面へのブリードアウトを遮断)、

(14)プラスチック表面の酸化防止膜、(15)透明樹脂をコア層としたクラッド層を傾斜膜で形成した光ファイバー、(16)同上で透明樹脂を太径のロッドとしたロッドレンズ、などを挙げることができる。

【0073】

【実施例】次に、本発明を実施例によりさらに詳細に説明するが、本発明は、これらの例によってなんら限定されるものではない。

【0074】実施例1

(1)有機-無機複合膜の形成

メタクリル酸メチル〔和光純薬工業(株)製〕11.8gおよび3-メタクリロキシプロピルトリメトキシシラン〔信越化学工業(株)製〕0.5gを混合し、よく攪拌したのち、これに、2, 2'-アゾビスイソブチロニトリル〔和光純薬工業(株)製〕0.2gを添加し、攪拌しながら70℃で2.5時間反応させた。反応終了後、室温まで冷却したのち、アセトン246ミリリットル中に重合物を溶解させ、さらにエタノール123ミリリットルを加え、(A)成分の有機高分子化合物の溶液(以下、高分子溶液と称す。)を調製した。

【0075】一方、テトラエトキシシラン〔和光純薬工業(株)製〕61.5ミリリットル中に、塩酸0.05g/ミリリットル濃度の塩酸・イソプロパノール溶液30.8ミリリットルを攪拌しながら滴下し、室温で5時間攪拌を続けた。この無機成分溶液を、上記で得た高分子溶液中に静かに滴下し、室温で4時間攪拌したのち、アセトン515ミリリットルで希釈し、よく攪拌後、さらにエタノール738ミリリットルで希釈して塗布液を調製した。この塗布液をスピンコート法(1500rpm, 10秒間)にて、ポリメチルメタクリレート基板上に塗布し、70℃で12時間加熱乾燥処理することにより、厚さ0.6μmの有機-無機複合膜を形成させた。

【0076】(2)評価

(イ)傾斜性

上記(1)で得た有機-無機複合膜に、XPS装置「PHI-5600」〔アルバック・ファイ(株)製〕を用い、アルゴン・スパッタリング(4kV)を5分間隔で施して膜を削り、膜表面の炭素原子とケイ素原子の含有率を、X線光電子分光法により測定し、傾斜性を調べた。図1に、スパッタリング時間(膜の深さと関係する)と炭素原子およびケイ素原子の含有率との関係をグラフで示す。この図から、優れた傾斜性を有することが分かる。

【0077】(ロ)二酸化チタン中間膜用途の耐久性

上記(1)で得られた有機-無機複合膜を中間膜とし、この上に「STS-01」〔石原産業(株)製〕を蒸留水で3倍に希釈した光触媒コート剤を、スピンコート法(1500rpm, 10秒間)により塗布し、70℃で12時間乾燥固着させることにより、厚さ0.4μmの二酸化チタンコート膜を形成した。これを密閉シリカガラス容器内に入れ、温度60℃、相対湿度50%に調整したのち、ブラックライトを用いて光照射(光量2.0mW/cm²)し、紫外線照射に伴う可視光(400~800nm)での透過率の経時変化を測定した。図12に、可視光領域での該膜の透過率スペクトルの経時変化を示す。

【0078】また、紫外線照射時間に対する波長500nmでの透過率の経時変化から、その透過率の減少速度

を数値化し、これを耐久性評価の指数とした。図13に、紫外線照射日数と波長500nmでの透過率の減少量との関係をグラフで示す。図12及び図13から、優れた耐久性を有することが分かる。

【0079】〈促進曝露試験〉さらに、この膜をサンシャインウェザーメータ（機内温度60℃、スプレーサイクル120分中18分）を用いて促進曝露試験を行い、光触媒による劣化の度合いを光線透過率の変化及び外観の変化により調べた。図14にサンシャインウェザーメータの曝露時間に対する可視光線透過率の変化を示す。500nmの光線透過率は、試験前の90%に対し、20日間経過後は87%とほぼ維持しており、また外観上の変化もなく、良好な耐候性を示した。

【0080】実施例2

実施例1において、ポリメチルメタクリレート基板の代わりにポリスチレン基板を用いた以外は、実施例1と同様にして、有機-無機複合膜を形成させた。この膜について、実施例1と同様にして傾斜性を評価した。図2に、スパッタリング時間と炭素原子およびケイ素原子の含有率との関係をグラフで示す。この図から、優れた傾斜性を有することが分かる。

【0081】実施例3

実施例1において、ポリメチルメタクリレート基板の代わりにポリエチレンテレフタレートフィルムを用いた以外は、実施例1と同様にして有機-無機複合膜を形成させた。この膜について実施例1と同様にして、傾斜性を評価した。図3に、スパッタリング時間と炭素原子およびケイ素原子の含有率との関係をグラフで示す。この図から、優れた傾斜性を有することが分かる。

【0082】実施例4

実施例1において、ポリメチルメタクリレート基板の代わりにポリプロピレンフィルムを用いた以外は、実施例1と同様にして有機-無機複合膜を形成させた。この膜について実施例1と同様にして、傾斜性を評価した。図4に、スパッタリング時間と炭素原子およびケイ素原子の含有率との関係をグラフで示す。この図から、優れた傾斜性を有することが分かる。

【0083】実施例5

実施例1において、塗布液をエタノール/アセトン混合溶剤（容量比1/1）で5倍に希釈して用い、かつスピンコート法の代わりにディップコート法（引上げ速度0.5cm/分）を採用した以外は、実施例1と同様にして有機-無機複合膜を形成させた。この膜について実施例1と同様にして、傾斜性を評価した。図5に、スパッタリング時間と炭素原子およびケイ素原子の含有率との関係をグラフで示す。この図から、優れた傾斜性を有することが分かる。

【0084】実施例6

実施例1において、テトラエトキシシラン61.5ミリリットルの代わりに、テトライソプロポキシチタン〔和

光純薬工業（株）製〕84.0ミリリットルを用いた以外は、実施例1と同様にして有機-無機複合膜を形成させた。この膜について実施例1と同様にして、傾斜性を評価した。図6に、スパッタリング時間と炭素原子およびチタン原子の含有率との関係をグラフで示す。この図から、優れた傾斜性を有することが分かる。

【0085】実施例7

実施例1において、ポリメチルメタクリレート基板の代わりにポリカーボネート基板（三菱エンジニアリングプラスチック（株）製ユーピロン、厚み400μm）を用いた以外は、実施例1と同様にして有機-無機傾斜複合膜を形成させた。この膜について、実施例1と同様にして傾斜性を評価した。図15に、スパッタリング時間と炭素原子およびケイ素原子の含有率との関係をグラフで示す。この図から、優れた傾斜性を有することが分かる。

【0086】実施例8

（1）有機-無機複合膜の形成

〔（A）成分の調製〕100ミリリットルのガラス製容器にメタクリル酸メチル〔和光純薬工業（株）製（以後MMAと略記することがある）〕10.92g及び3-メタクリロキシプロピルトリメトキシシラン〔信越化学工業（株）製（以後MPTMSと略記することがある）〕

2.71gを入れて混合し、よく攪拌したのち、これに、2,2'-アゾビスイソブチロニトリル〔和光純薬工業（株）製〕0.2gを添加し、蓋をして密閉した。この容器をウォーターバス中に置き、マグネチックスターラーで攪拌しながら、70℃で2.5時間ラジカル重合反応を行った。反応終了後、重合物を室温まで冷却したのち、アセトン100ミリリットル中に重合物1.0gを溶解させ、（A）成分の有機高分子化合物の溶液（以下、高分子溶液と称す）を調製した。

【0087】〔（B）成分の調製〕一方、テトラエトキシシラン〔和光純薬工業（株）製試薬特級（以後TEOSと略記することがある）〕12gをエタノール100ミリリットル中に溶解した溶液に、濃塩酸3.1gとエタノール5ミリリットルからなる溶液を攪拌しながら徐々に滴下した。この混合溶液を室温で5時間攪拌し、（B）成分の無機成分溶液とした。

【0088】〔傾斜膜塗布液の調製〕高分子溶液10ミリリットルをアセトン40ミリリットルで希釈し、よく攪拌後、エタノール40ミリリットルを添加し、さらに無機成分溶液10ミリリットルを加え、攪拌して傾斜膜塗布液を調製した。

【0089】〔傾斜膜のスピンコート〕スピンコーターの回転カップ上に、12cm角のポリエチレンテレフタレート（PET）フィルム〔東レ（株）製ルミラーT-60、フィルム厚み188μm〕を固定し、フィルムの表面を濡らすように上記傾斜膜塗布液をフィルム上に載せ、フィルム全体を濡らし終わってから5秒後、回転カップを1500rpm、10秒間にて回転させ、塗布液

をスピンコートした。塗布されたフィルムをオープン中70℃で12時間加熱乾燥処理することにより、厚さ0.2μmの有機-無機複合膜をPETフィルム上に形成させた。

【0090】(2) アンモニア処理

上記フィルムを0.05Nのアンモニア水に5分間浸漬したのち、オープン中70℃で12時間加熱乾燥した。

【0091】(3) 評価

【光触媒酸化チタンコート剤の塗布】この有機-無機複合膜上に酸化チタン光触媒コート剤（日本曹達(株)製ピストレータNDC-200C）をイソプロパノールで10倍に希釈した液を、スピンコート法（1500rpm、20秒間）にて塗布し、オープン中80℃で12時間乾燥及び熱処理を行うことにより、厚さ0.15μmの酸化チタンコート膜を形成した。

【0092】【促進曝露試験】上記光触媒酸化チタンがコーティングされたフィルムについて、サンシャインウェザーメーター（機内温度60℃、スプレーサイクル120分中18分）を用いて促進曝露試験を行い、光触媒による劣化の度合いを光線透過率の変化及び外観の変化により調べた。図16にサンシャインウェザーメーターの曝露時間に対する可視光線透過率の変化を示す。500nmの光線透過率は、試験前の81%に対し、20日間経過後は79%とほぼ維持しており、また外観上の変化もなく、良好な耐候性を示した。

【0093】また上記(1)でコーティングしたフィルムをオートクレーブ中にて、130℃、1.7kgf/cm²の条件で3時間加熱処理したものについて、上記と同様にして光触媒酸化チタンコート剤を塗布し、サンシャインウェザーメーターによる曝露試験を行ったところ、アンモニア処理フィルムと同様に良好な結果が得られた。

【0094】実施例9

【傾斜中間膜のコロナ放電処理】実施例8において、PETフィルム〔東レ(株)製ルミラーT-60、フィルム厚み188μm〕上に傾斜膜塗布液をコーティングした後、コロナ放電処理装置（春日電機(株)製、印加電圧150V、電流15A）で3秒間処理した以外は、実施例8と同様にして光触媒酸化チタンがコートされたフィルムを得た。このフィルムをサンシャインウェザーメーターによる促進曝露試験を行った。図17にサンシャインウェザーメーターの曝露時間に対する可視光線透過率の変化を示す。500nmの光線透過率は、試験前の81%に対して、20日間経過後は79%とほぼ維持しており、また外観上の変化もなく、良好な耐候性を示した。

【0095】実施例10

実施例8において、MMA/MPTMSのモル比を10/1として、(A)成分の10g/リットルのアセトン溶液を調製した。一方、TEOS12gおよび濃塩酸2.5g、エタノール5gの混合溶液を滴下し、10時

間攪拌して無機成分液とした。(A)成分液の3ミリリットルとアセトン22ミリリットル及び無機成分液4ミリリットルを混合し、さらにn-ヘキサノール21ミリリットルを加えよく攪拌した。この液にPETフィルムを浸漬し、15cm/分の速度で引き上げてコーティングした。このコーティングフィルムの傾斜性を実施例1と同様に測定した。図18に、スパッタリング時間とケイ素原子の含有率との関係を示す。この図から優れた傾斜性を有することが分かる。

【0096】実施例11

実施例8において、MMA/MPTMSのモル比を1/1、20/1、100/1として、(A)成分が10g/リットルのアセトン溶液を調製した。一方、TEOS12gおよび濃塩酸2.5g、エタノール5gの混合溶液を滴下し、10時間攪拌して無機成分液とした。

(A)成分液の3ミリリットルとアセトン22ミリリットル及び無機成分液4ミリリットルを混合し、さらにn-ヘキサノール21ミリリットルを加えよく攪拌した。この液にPETフィルムを浸漬し、5.0cm/分の速度で引き上げてコーティングした。このコーティングフィルムの傾斜性を実施例1と同様に測定した。図19に、上記3種類のMMA/MPTMS（モル比）について、スパッタリング時間とケイ素原子の含有率との関係を示す。この図からMMA/MPTMSのモル比の変化により、傾斜の傾きを制御できることが分かる。

【0097】実施例12

実施例8において、MMA/MPTMSのモル比を10/1として、(A)成分が10g/リットルのアセトン溶液を調製した。一方、TEOS12gおよび濃塩酸2.5g、エタノール5gの混合溶液を滴下し、10時間攪拌して無機成分液とした。(A)成分液の1ミリリットルとアセトン4ミリリットルに無機成分液を任意量加え、無機成分濃度が1、2、4、6重量%の塗布液を調製した。この液を実施例8と同様の方法でPETフィルム上のスピンコートし、有機-無機複合傾斜膜を得た。この傾斜膜の傾斜性を実施例1と同様に測定した。図20に、上記4種類の無機成分濃度の傾斜膜における、スパッタリング時間とケイ素原子の含有率との関係を示す。この図から無機成分濃度の変化により、傾斜の傾きを制御できることが分かる。

【0098】実施例13

実施例4と同様の方法で3cm角の黒色塗料が塗られた自動車鋼板（アクリル/メラニン樹脂コート）上に傾斜膜塗布液をコーティングし、オープン中70℃、12時間乾燥した。得られた膜付自動車鋼板をプラズマジェット（春日電機(株)製PJ-1）で3秒間処理したのち、酸化チタン光触媒コート剤（日本曹達(株)製NDC-200C）1gを濃塩酸0.08gと2-プロパノール9gにより希釈したものをスピンコート法（1500rpm、20秒間）にて塗布し、80℃のオープン中1時間

乾燥および熱処理を行うことにより厚さ0.2 μm の酸化チタンコート膜を形成した。上記光触媒がコーティングされた自動車鋼板を、サンシャインウェザーメーター（試験機内温度60℃、スプレーサイクル120分中18分）により促進曝露試験を行い、水の接触角及び外観の変化を調べた。20日間経過後に水接触角の測定を行*

表1

		曝 露 時 間 (hr)					
		0	60	120	180	240	420
傾斜膜	接触角(度)	<3	<3	<3	<3	<3	<3
	外 観	良好	良好	良好	良好	良好	良好

【0100】比較例1

実施例1における高分子溶液の調製において、3-メタクリロキシプロピルトリメトキシシランを用いずに、メタクリル酸メチルの量を12gに変更した以外は、実施例1と同様にして塗膜を形成させた。この膜について実施例1と同様にして傾斜性を評価した。図7に、スパッタリング時間と炭素原子およびケイ素原子の含有率との関係をグラフで示す。この図から分かるように、傾斜性を有する膜が得られなかった。

【0101】比較例2

実施例1において、ポリメチルメタクリレート基板の代わりにガラス基板を用いた以外は、実施例1と同様にして塗膜を形成させた。この膜について実施例1と同様にして傾斜性を評価した。図8に、スパッタリング時間と炭素原子およびケイ素原子の含有率との関係をグラフで示す。この図から分かるように、傾斜性を有する膜が得られなかった。

【0102】比較例3

市販のアクリルシリコーン樹脂溶液「GS-1020」〔東亜合成(株)製〕6.5gをトルエン/イソプロパノール混合溶剤（容量比1/1）20gに加え、攪拌混合したものを、ポリメチルメタクリレート基板上にスピンコート法（1500rpm、10秒間）で塗布し、70℃で12時間乾燥させて、中間膜としての塗膜を形成させた。この膜の二酸化チタン中間膜用途の耐久性について、実施例1と同様にして評価した。

【0103】図9に、可視光領域での該膜の透過率スペクトルの経時変化を示し、図13に、紫外線照射日数と波長500nmでの透過率の減少量との関係をグラフで示す。図9および図13から分かるように、この膜は良好な耐久性を示さなかった。

【0104】比較例4

市販の無機接着剤「エチルシリケート40」〔コルコート(株)製〕8.1gを、トルエン/イソプロパノール混合溶剤（容量比1/1）20gに加え、攪拌混合したものを、ポリメチルメタクリレート基板上にスピンコート法（1500rpm、10秒間）で塗布し、70℃で12時間乾燥させて、中間膜としての塗膜を形成させ

＊ったところ、接触角3°未満であり、試験前と比べて表面の超親水性に変化はなかった。また干渉縞や白化も見られず良好な耐久性を示した。表1に、曝露時間と傾斜膜の接触角および外観との関係を示す。

【0099】

【表1】

た。この膜の二酸化チタン中間膜用途の耐久性について、実施例1と同様にして評価した。

【0105】図10に、可視光領域での該膜の透過率スペクトルの経時変化を示し、図13に、紫外線照射日数と波長500nmでの透過率の減少量との関係をグラフで示す。図10および図13から分かるように、この膜は良好な耐久性を示さなかった。

【0106】比較例5

市販のアクリルシリコーン樹脂溶液「GS-1020」〔東亜合成(株)製〕5.0gをトルエン/イソプロパノール混合溶剤（容量比1/1）10gに加え、攪拌混合したものに、市販の無機接着剤「エチルシリケート40」〔コルコート(株)製〕1.9gをゆっくり滴下し、攪拌混合した。さらに、トルエン/イソプロパノール混合溶剤（容量比1/1）10gを添加し、攪拌混合して塗布液を調製した。この塗布液を、ポリメチルメタクリレート基板上にスピンコート法（1500rpm、10秒間）で塗布し、70℃で12時間乾燥させて、中間膜としての塗膜を形成させた。この膜の二酸化チタン中間膜用途の耐久性について、実施例1と同様にして評価した。

【0107】図11に、可視光領域での該膜の透過率スペクトルの経時変化を示し、図13に、紫外線照射日数と波長500nmでの透過率の減少量との関係をグラフで示す。図11および図13から分かるように、この膜は多少良好な耐久性を示すが、やはり透過率の減少が確認された。

【0108】比較例6

実施例8において、MPTMSを使用せず、(A)成分と(B)成分が化学結合していない有機-無機複合膜用塗布液を合成した。すなわち、50ミリリットルのガラス製容器にメタクリル酸メチル〔和光純薬工業(株)製〕12gおよび2,2'-アゾビスイソプロピロニトリル〔和光純薬工業(株)製〕0.2gを添加し、蓋をして密閉した。この容器をウォーターバス中に置き、マグネチックスターラーで攪拌しながら、75℃で2.5時間ラジカル重合反応を行った。反応終了後、重合物を室温まで冷却したのち、アセトン20ミリリットル中に上記重

合物0.2gを溶解させ、MP TMSを含まない高分子溶液を調製した。

【0109】一方、実施例8と同様にテトラエトキシシランを使用して(B)成分の無機成分溶液を得た。以後、実施例8と同様に塗布液を調製して、PETフィルムにコーティングし、さらに光触媒酸化チタンコート剤を塗布して得られたフィルムのサンシャインウェザーメーターによる促進曝露試験の結果を図21に示す。500nmにおける光線透過率は、試験前の83%から5日間経過後ですでに光線透過率が45%まで低下し、外観上においても白化が生じて膜が劣化していることが分かった。

【0110】比較例7

実施例1において、有機-無機複合膜塗布液の代わりに、市販の光触媒酸化チタンコート剤用アンダーコート剤(日本曹達(株)製ヒストレータNDC-100A)をアクリル基板に塗布した以外は、実施例1と同じ方法で光触媒酸化チタンがコートされたフィルムを得た。このフィルムをサンシャインウェザーメーターによる促進曝露試験を行った。図22にサンシャインウェザーメーターの曝露時間に対する可視光線透過率の変化を示す。500nmにおける光線透過率は、試験前の76%から5日間経過後ですでに光線透過率が57%まで低下し、外観上においても白化が生じて膜が劣化していることが分かった。

【0111】比較例8

実施例8において、有機-無機複合膜塗布液の代わりに市販の光触媒酸化チタンコート剤用アンダーコート剤を用いた以外は、実施例8と同じ方法で光触媒酸化チタンがコートされたフィルムを得た。このフィルムをサンシャインウェザーメーターによる促進曝露試験を行った。図23にサンシャインウェザーメーターの曝露時間に対する可視光線透過率の変化を示す。500nmにおける光線透過率は、試験前の74%から20日間経過後で光線透過率が66%まで低下し、外観上においても白化が生じて膜が劣化していることが分かった。

【0112】実施例14

〔(A)成分の調製〕メチルメタクリレート21.8gおよび3-メタクリロキシプロピルトリメトキシシラン5.41gを混合し、よく攪拌したのち、これに2,2'-アゾビスイソブチロニトリル0.4gを添加し、攪拌しながら70℃で2.5時間反応させた。放冷後、得られた重合物の内、4gを2リットルのメチルエチルケトンに溶解し、(A)成分の高分子溶液を調製した。

【0113】〔(B)成分の調製〕一方、テトラエトキシシラン480gとエタノール400gの混合溶液中に、濃硝酸40gとエタノール200gと水460gの混合液を攪拌しながらゆっくり滴下し、室温で5時間攪拌を継続し、(B)成分の無機成分溶液とした。

【0114】〔傾斜膜塗布液の調製〕

(A)成分の高分子溶液にエチルセロソルブ1.5リットルを添加し、攪拌混合したのち、これに(B)成分の無機成分溶液500gを添加し、よく攪拌して傾斜膜塗布液を調製した。

【0115】〔傾斜膜のバーコート〕ヒラノテクシード(株)社製の「マルチコーターM200」にてキスマイヤーパー法(線径0.1mm、ライン速度10m/min、乾燥温度120℃)にて、東レ(株)社製PETフィルム「ルミラーT-60」(厚み50μm、幅330mm)に塗工し、厚み0.1μmの有機-無機複合膜を形成させた。この膜について実施例1と同様にして傾斜性を評価した。図24にスパッタリング時間と炭素原子およびケイ素原子の含有率との関係をグラフに示す。この図から優れた傾斜性を有することが分かる。

【0116】実施例15

実施例14と同様にして得られた重合物の内、2gを1リットルのメチルイソブチルケトンに溶解して(A)成分の高分子溶液とした。この高分子溶液に、1-ブタノール0.8リットルを添加し、攪拌混合したのち、実施例14における(B)成分の無機成分溶液200gを添加し、よく攪拌して傾斜膜塗布液を調製した。

【0117】これを、アネスト岩田(株)社製スプレーガン「W-88シリーズ」により、エア圧0.2MPa、スプレー距離15cm、スプレー運行速度15m/minにて、三菱レーヨン(株)社製アクリル板「アクリライト」(厚み2mm、300mm×300mm)に塗工し、80℃で乾燥処理して、厚み0.15μmの有機-無機複合膜を形成させた。この膜について実施例1と同様にして傾斜性を評価した。図25にスパッタリング時間と炭素原子およびケイ素原子の含有率との関係をグラフに示す。この図から優れた傾斜性を有することが分かる。

【0118】実施例16

実施例14と同様にして得られた重合物の内、1gを松本製薬工業(株)製テトラインシアナトシラン「オルガックス-Si400」56gを1リットルのトルエンに溶解して傾斜膜塗布液を調製した。

【0119】これを、アネスト岩田(株)社製スプレーガン「W-88シリーズ」により、エア圧0.2MPa、スプレー距離15cm、スプレー運行速度15m/minにて、三菱レーヨン(株)社製アクリル板「アクリライト」(厚み2mm、300mm×300mm)に塗工し、25℃で乾燥処理して、厚み0.12μmの有機-無機複合膜を形成させた。この膜について実施例1と同様にして傾斜性を評価した。図26にスパッタリング時間と炭素原子およびケイ素原子の含有率との関係をグラフに示す。この図から優れた傾斜性を有することが分かる。

【0120】実施例17

実施例14と同様にして得られた重合物の内、1gを東

燃(株)製ポリシラザン「L110(20重量%キシレン溶液)」0.29リットルを0.71リットルのキシレンに溶解して傾斜膜塗布液を調製した。

【0121】これを、スピンコーター(1500rpm、15秒)にてPETフィルム「東レミラーT-60」に塗工し、80℃で1時間、95℃、80%RHで3時間乾燥処理して、厚み0.12μmの有機-無機複合膜を形成させた。この膜について実施例1と同様にして傾斜性を評価した。図27にスパッタリング時間と炭素原子およびケイ素原子の含有率との関係をグラフに示す。この図から優れた傾斜性を有することが分かる。

【0122】実施例18

【(A)成分の調製】スチレン(和光純薬工業)11.86gと3-メタクロキシプロビルトリメトキシシラン1.42gを容量50ミリリットルのガラス容器に入れ、2,2'-アゾビスイソブチロニトリル0.2gを加えて、攪拌して完全に溶解させた。次に70℃に調整した湯浴にて、この容器を5時間加熱し、スチレンを重合させた。得られたポリスチレン共重合体0.2mgを、別のガラス容器に移し、テトラヒドロフラン溶媒200ミリリットルに溶解させ、(A)成分の高分子溶液を調製した。

【0123】〔傾斜膜の調製〕容量100ミリリットルのガラス容器にテトラヒドロフラン40ミリリットル、エタノール40ミリリットルを入れ、これに上記高分子溶液と実施例1で得られた無機成分溶液10ミリリットルずつ加え、傾斜膜塗布液を調製した。

【0124】〔傾斜膜のスピンコート〕上記塗布液を用いて、実施例1に準ずる方法で、スピンコート法によりPET基板上に塗布し、乾燥させて有機-無機複合膜を形成させた。この膜について実施例1と同様にして傾斜性を評価した。図28にスパッタリング時間と炭素原子およびケイ素原子の含有率との関係をグラフに示す。この図から優れた傾斜性を有することが分かる。

【0125】実施例19 導電性フィルム

(1)有機-無機複合膜の形成

メチルメタクリレート10.92gおよび3-メタクロキシプロビルトリメトキシシラン2.71gを混合し良く攪拌した後、これに、2,2'-アゾビスイソブチロニトリル0.2gを添加し、攪拌しながら75℃で3時間反応させた。得られた重合物の内1.0gをアセトン100ミリリットルに溶解させ、(A)成分の有機高分子化合物の溶液(以下、高分子溶液と称す。)を調製した。

【0126】一方、テトラエトキシシラン12gをエタノール10ミリリットルに溶解した溶液に、濃塩酸3.1gとエタノール5ミリリットルからなる溶液を攪拌しながら徐々に滴下した。この混合溶液を室温で5時間攪拌し、(B)成分の無機成分溶液を得た。アセトン40ミリリットルに高分子溶液10ミリリットルを混合し均

一に攪拌した後、エタノール40ミリリットルを添加し、更に、無機成分10ミリリットルを加え、均一になるまで攪拌した。

【0127】この塗布液をスピンコート法(1500rpm、10秒)にて厚みが0.188mmのポリエチレンテレフタレートフィルム上に塗布し、40℃で12時間加熱乾燥することにより、基板上に有機-無機複合膜を形成させた。この膜のXPS(アルバック・ファイ社製、PHI-5600)のデプスプロファイル測定により、炭素とケイ素の含有比率を測定し、傾斜性を調べた。図29に、スパッタリング時間と炭素原子およびケイ素原子の含有率との関係をグラフで示す。この図から優れた傾斜性を有することが判る。

【0128】(2)導電性フィルムの作製

(1)で得られた膜上に、酸化インジウム90重量%及び酸化第二スズ10重量%からなる酸化物ターゲットを用い、アルゴンと酸素の混合ガス(容積比で99:1)雰囲気下で、DCマグネトロンスパッタ装置(島津製作所、HS-720)にて厚さ40nmの透明導電膜を形成させ、導電性フィルムを作製した。得られた導電性フィルムを用い、その特性としてシート抵抗値、光線透過率、基盤目剥離試験、耐熱試験を以下の方法に従って調べた。その結果を表2にまとめた。

【0129】(イ)シート抵抗値

片面に形成された透明導電膜シート抵抗値(Ω/\square)を抵抗率計を用いて測定した。

(ロ)光線透過率

分光光度計(島津製作所、UV-2100)を用い、550nmの光線透過率(%)を測定した。

(ハ)基盤目剥離試験

JIS K5400に準じ、基盤目テープ法を実施した。各試験片の塗膜面にロータリーカッターにて1mm角の基盤目を100マス付け、ニチバン製セロテープ(登録商標)を圧着させた後、800mm/minの速度で180度の剥離試験を実施した。100マスのうち剥離の有無を数えることにより密着性の評価を行った。

【0130】(ニ)耐熱性

試験片をオープン中で、70℃で2時間保持後、-30℃に2時間かけて降温し、その後-30℃で2時間保持し、再び70℃まで2時間かけて昇温する過程を5サイクル行う、ヒートサイクル試験を実施した。評価は、シート抵抗値の測定ならびに基盤目剥離試験により、塗膜の密着性(100マス中の剥離の有無)を確認することにより行った。

【0131】実施例20

実施例7で得られた有機-無機複合傾斜膜つきポリカーボネートフィルムに対して、実施例19と同様の方法で導電性フィルムを作製した。表2にこの導電性フィルムの特性を示す。

【0132】実施例21

テトラエトキシシラン8.33gとメチルトリメトキシシラン1.36gをエタノール10ミリリットルに溶解した溶液に、濃塩酸3.1gとエタノール5ミリリットルからなる溶液を攪拌しながら徐々に滴下した。この混合溶液を室温で5時間攪拌し、無機成分溶液を得た。

【0133】アセトン40ミリリットルに実施例19の(A)高分子溶液10ミリリットルを混合し均一に攪拌した後、エタノール40ミリリットルを添加し、更に、無機成分溶液10ミリリットルを加え、均一になるまで攪拌した以外は、実施例19と全く同操作にて導電性フィルムを作製した。

【0134】図30に、ITO膜をコーティングする前の有機-無機複合膜のXPS(アルバック・ファイ社製、PHI-5600)のデプスプロファイル測定により、炭素とケイ素の含有比率を測定し、傾斜性を調べた結果を記載した。表2にこの導電性フィルムの特性を示す。

【0135】比較例9

実施例19において、メチルメタクリレート12gに、2,2'-アゾビスイソブチロニトリル0.2gを添加*20

表2

	導電性フィルムの特性				
	シート抵抗 (Ω/\square)	光線 透過率 (%)	基盤目 剥離試験	耐熱性	
				シート抵抗 (Ω/\square)	基盤目 剥離試験
実施例19	300	85	94/100	320	92/100
実施例20	280	83	100/100	280	100/100
実施例21	280	85	95/100	280	93/100
比較例9	310	84	50/100	1300	40/100
比較例10	300	85	100/100	1850	35/100

【0139】表2から分かるように、本発明の複合傾斜膜を中間膜として用いた実施例の導電性フィルムは、耐熱試験後においても、導電性および密着性はほとんど変わらないが、比較例のものは、耐熱試験後に、導電性および密着性共に大きく低下している。

【0140】実施例22 ハードコートフィルム

実施例8において、基材フィルムをポリカーボネートフィルムに代えた以外は、実施例8と同様の方法で、有機-無機複合傾斜膜つきフィルムを得た。これに、(株)日本ダクロシャムロック製シリコンハードコート剤[ゾルガードNP730]を、乾燥後の膜厚が4 μ mとなるようにパーコーターを用いて成膜し、その後80℃で2時間の硬化処理を行い、所望のハードコート膜付き基材を得た。なお、ハードコート前のフィルムについて、鉛筆硬度を測定したところ、ポリカーボネートフィルムのみはF、複合傾斜膜を設けたフィルムではHであった。このハードコート膜付き基材について以下の試験を実施した。結果を表3にまとめた。

【0141】(1) 密着性

*し、攪拌しながら75℃で3時間反応させて、得られた重合物の内1.0gをアセトン100ミリリットルに溶解させ、ポリメチルメタクリレート化合物の溶液を調製した以外は、実施例19と全く同操作を行い導電性フィルムを作製した。

【0136】図31に、ITO膜をコーティングする前の有機-無機複合膜のXPS(アルバック・ファイ社製、PHI-5600)のデプスプロファイル測定により、炭素とケイ素の含有比率を測定し、傾斜性を調べた結果を記載した。表2にこの導電性フィルムの特性を示す。

【0137】比較例10

比較例9にて調製したポリメチルメタクリレート化合物の溶液10ミリリットルをアセトン20ミリリットルとエタノール20ミリリットルにて希釈し塗布液とした以外は実施例19と全く同操作にて導電性フィルムを作製した。表2にこの導電性フィルムの特性を示す。

【0138】

【表2】

JIS K5400に準じ、基盤目テープ法を実施した。各試験片の塗膜面にロータリーカッターにて1mm角の基盤目を100マス付け、ニチバン製セロテープを圧着させた後、300mm/minの速度で180度の剥離試験を実施した。100マスのうち剥離の有無を数えることにより密着性の評価を行った。

【0142】(2) 膜硬度

JIS K5400に準じ、ヨシミツ精機(株)製、鉛筆ひっかけ試験機により鉛筆硬度試験を実施し、塗膜の傷の有無により膜硬度を評価した。

【0143】(3) 耐摩耗性

ヨシミツ精機(株)製、テーバー式摩耗試験機により、塗膜の耐摩耗試験を実施した(試験条件:摩耗回数200回、荷重500g、摩耗輪CS-10F)。試験後の曇り度(ヘイズ値:ΔH%)により耐摩耗性を評価した。

【0144】(4) 耐熱性

試験片をオープン中で、70℃で2時間保持後、-30℃に2時間かけて降温し、その後-30℃で2時間保持し、再び70℃まで2時間かけて昇温する過程を5サイ

クル行、ヒートサイクル試験を実施した。評価は、碁盤目テープ法により、塗膜の密着性（100マス中の剥離の有無）を確認することにより行った。

【0145】実施例23、24

基板を、厚み0.4mmのポリカーボネートフィルムから実施例19で作製した厚み0.188mmのポリエチレンテレフタレートフィルムに傾斜膜をコートしたフィルム（実施例23）ならびに、厚み0.2mmのアクリルフィルム（実施例24）に変更した以外は実施例22と全く同様の操作にて、ハードコート膜付き基材を得た。この膜付き基材の評価結果を表3にまとめた。図32に、実施例24のフィルムについて、ハードコーティング前の膜のXPS（アルバック・ファイ社製、PHI-5600）のデプスプロファイル測定により、炭素とケイ素の含有比率を測定し、傾斜性を調べて結果を記載した。

【0146】なお、ポリエチレンテレフタレートフィルムおよびそれに複合傾斜膜を設けたフィルムの鉛筆硬度は、それぞれ3Hおよび4Hであり、アクリルフィルムおよびそれに複合傾斜膜を設けたフィルムの鉛筆硬度は、それぞれ4Hおよび5Hであった。

【0147】実施例25

アセトン40ミリリットルに実施例8の（A）成分の高分子溶液10ミリリットルを混合し均一に攪拌した後、エタノール30ミリリットルを添加し、更に、実施例8の（B）成分の無機成分溶液20ミリリットルを加え、均一になるまで攪拌し、さらにフィルム基材をポリカー-

* ポネートフィルムに代えた以外は、全く実施例8と同様の操作にて、ハードコート膜付き基板を得た。この膜付き基材の評価結果を表3にまとめた。図33に、ハードコート前の膜のXPS（アルバック・ファイ社製、PHI-5600）のデプスプロファイル測定により、炭素とケイ素の含有比率を測定し、傾斜性を調べて結果を記載した。

【0148】比較例11

実施例8において、メチルメタクリレート12gに、2,2'-アゾビスイソブチロニトリル0.2gを添加し、攪拌しながら75℃で3時間反応させて、得られた重合物の内1.0gをアセトン100ミリリットルに溶解させ、ポリメチルメタクリレート化合物の溶液を調製して高分子溶液とし、フィルム基材をポリカーボネートフィルムとした以外は実施例8と全く同操作を行い、ハードコート膜付き基材を作製した。この膜付き基材の評価結果を表3にまとめた。

【0149】比較例12

厚み0.4mmのポリカーボネートフィルムに、(株)日本ダクロシャムロック製シリコンハードコート剤〔ゾルガードNP730〕を、乾燥後の膜厚が4μmとなるようにパーコーターにて成膜し、その後80℃で2時間の硬化処理を行い、所望のハードコート膜付き基材を得た。この膜付き基材の評価結果を表3にまとめた。

【0150】

【表3】

表3

	密着性	膜硬度	耐摩耗性 (ΔH%)	耐熱性
実施例22	100/100	4H	8	100/100
実施例23	94/100	6H	8	92/100
実施例24	100/100	6H	6	100/100
実施例25	100/100	4H	8	100/100
比較例11	44/100	3H	28	34/100
比較例12	10/100	2H	55	0/100

【0151】表3から分かるように、傾斜膜をハードコート層のプライマーとして用いた場合（実施例22～25）、傾斜膜は構造体中に無機成分及び有機成分を含み、かつ無機成分から有機成分にかけて傾斜構造を有しているため、有機基材とシリコン系ハードコート層の双方との密着性に極めて優れており、ハードコート層の性能を十分に発揮させ得る。

【0152】これに対し、（A）成分のメチルメタクリレートポリマーと（B）成分の無機成分との間に化学結合を有しないアクリルシリコンをハードコート層のプライマー層として用いた場合（比較例11）、無機成分と有機成分とが化学結合していないため、傾斜構造にな

らず無機成分と有機成分との界面の密着性が低く、性能に劣る。また、プライマーが無い場合（比較例12）、ハードコート剤自身が無機材料のシリコン系であるため、有機基材との密着性に乏しく、性能に劣る。

【0153】実施例26 光記録媒体

実施例7で得られた傾斜膜付きポリカーボネートフィルムをスパッタ装置にセットし、傾斜膜の上に誘電体下地層（アンダーコート）として厚さ8μmのSiN層を成膜し、アンダーコート形成樹脂基板を得た。アンダーコート形成樹脂基板をスパッタ装置にセットし、アンダーコート上に光磁気記録層として厚さ10μmのTbDyFeCo層を成膜し、さらに誘電体保護層（トップコー

ト)として厚さ8 μ mのSiN層を成膜することにより、所望の光磁気記録媒体を得た。この光磁気記録媒体について以下の試験を実施した。結果を表4にまとめた。

【0154】(1) アンダーコートと基材フィルム間の密着性

JIS K5400に準じ、碁盤目テープ法を実施した。各試験片の塗膜面にロータリーカッターにて1mm角の碁盤目を100マス付け、ニチバン製セロテープを圧着させた後、300mm/minの速度で180度の剥離試験を実施した。100マスのうち剥離の有無を数えることにより密着性の評価を行った。また、試験片をオープン中で、70℃で2時間保持後、-30℃に2時間かけて降温し、その後-30℃で2時間保持し、再び70℃まで2時間かけて昇温する過程を5サイクル行う、ヒートサイクル試験を実施し、同様に密着性を測定した。

【0155】(2) 膜硬度

JIS K5400に準じ、ヨシミツ精機(株)製、鉛筆ひっかき試験機により鉛筆硬度試験を実施し、塗膜の傷の有無により膜硬度を評価した。

*

表4

	アンダーコートと樹脂基板との密着性		膜 硬 度
	ヒートサイクル前	ヒートサイクル後	
実施例26	100/100	95/100	H
実施例27	100/100	94/100	H
比較例13	81/100	65/100	H
比較例14	0/100	0/100	F

【0160】なお、70℃、90%RHの高温高湿下で40時間保持した後の各基板の反りを測定し、データの書き込みおよび読みとりとに支障がないかを調べたところ、実施例26、27および比較例13、14のいずれも問題はなかった。

【0161】

【発明の効果】本発明の有機-無機複合傾斜材料は、有機高分子化合物と金属系化合物との化学結合物を含有する有機-無機複合材料であって、該金属系化合物の含有率が材料の厚み方向に連続的に変化する成分傾斜構造を有し、新規な機能性材料として各種用途、特にコーティング剤として、塗膜、有機材料と無機または金属材料との接着剤および有機基材と無機系または金属系材料を含むコート層との間に介在させる中間膜用に好適である。

【図面の簡単な説明】

【図1】実施例1で得られた有機-無機複合膜におけるスパッタリング時間と炭素原子およびケイ素原子の含有率との関係を示すグラフである。

【図2】実施例2で得られた有機-無機複合膜におけるスパッタリング時間と炭素原子およびケイ素原子の含有率との関係を示すグラフである。

*【0156】実施例27

アセトン40ミリリットルに実施例19の(A)成分の高分子溶液10ミリリットルを混合し均一に攪拌した後、エタノール30ミリリットルを添加し、更に、実施例19の(B)成分の無機成分溶液20ミリリットルを加え、均一になるまで攪拌した操作以外は、全く実施例19と同様の操作にて、光磁気記録媒体を得た。この膜付き基材の評価結果を表4にまとめた。

【0157】比較例13

メチルメタクリレート12g、アゾビスイソブチロニトリル0.2gを混合、攪拌しながら75℃に保ち、3時間反応させて有機高分子成分を得た以外は、実施例26と同一の操作で光磁気記録媒体を得た。表4にこの光磁気記録媒体の特性を示す。

【0158】比較例14

ポリカーボネート基板に、有機-無機複合膜を形成することなく実施例26と同手法にて光磁気記録媒体を作成した。表4にこの光磁気記録媒体の特性を示す。

【0159】

【表4】

【図3】実施例3で得られた有機-無機複合膜におけるスパッタリング時間と炭素原子およびケイ素原子の含有率との関係を示すグラフである。

【図4】実施例4で得られた有機-無機複合膜におけるスパッタリング時間と炭素原子およびケイ素原子の含有率との関係を示すグラフである。

【図5】実施例5で得られた有機-無機複合膜におけるスパッタリング時間と炭素原子およびケイ素原子の含有率との関係を示すグラフである。

【図6】実施例6で得られた有機-無機複合膜におけるスパッタリング時間と炭素原子およびチタン原子の含有率との関係を示すグラフである。

【図7】比較例1で得られた塗膜におけるスパッタリング時間と炭素原子およびケイ素原子の含有率との関係を示すグラフである。

【図8】比較例2で得られた塗膜におけるスパッタリング時間と炭素原子およびケイ素原子の含有率との関係を示すグラフである。

【図9】比較例3で得られた塗膜における可視光領域での透過率スペクトルの経時変化を示すグラフである。

【図10】比較例4で得られた塗膜における可視光領域

での透過率スペクトルの経時変化を示すグラフである。

【図11】比較例5で得られた塗膜における可視光領域での透過率スペクトルの経時変化を示すグラフである。

【図12】実施例1で得られた有機-無機複合膜における可視光領域での透過率スペクトルの経時変化を示すグラフである。

【図13】実施例1で得られた有機-無機複合膜および比較例3~5で得られた塗膜における紫外線照射日数と波長500nmでの透過率の減少量との関係を示すグラフである。

【図14】実施例1で得られた、有機-無機複合膜を中間膜とし、二酸化チタンコート膜が設けられたフィルムのサンシャインウェザーメーターの曝露試験における可視光線透過率の変化を示すグラフである。

【図15】実施例7で得られた有機-無機複合膜におけるスパッタリング時間と炭素原子およびケイ素原子の含有率との関係を示すグラフである。

【図16】実施例8で得られた、有機-無機複合膜を中間膜とし、二酸化チタンコート膜が設けられたフィルムのサンシャインウェザーメーターの曝露試験における可視光線透過率の変化を示すグラフである。

【図17】実施例9で得られた、有機-無機複合膜を中間膜とし、二酸化チタンコート膜が設けられたフィルムのサンシャインウェザーメーターの曝露試験における可視光線透過率の変化を示すグラフである。

【図18】実施例10で得られた有機-無機複合膜におけるスパッタリング時間と炭素原子およびケイ素原子の含有率との関係を示すグラフである。

【図19】実施例11で得られた3種類の有機-無機複合膜におけるスパッタリング時間とケイ素原子の含有率との関係を示すグラフである。

【図20】実施例12で得られた4種類の有機-無機複合膜におけるスパッタリング時間とケイ素原子の含有率との関係を示すグラフである。

【図21】比較例6で得られた、有機-無機複合膜を中間膜とし、二酸化チタンコート膜が設けられたフィルムのサンシャインウェザーメーターの曝露試験における可視光線透過率の変化を示すグラフである。

【図22】比較例7で得られた、アンダーコート剤を中間膜とし、二酸化チタンコート膜が設けられたフィルムのサンシャインウェザーメーターの曝露試験における可視光線透過率の変化を示すグラフである。

【図23】比較例8で得られた、アンダーコート剤を中間膜とし、二酸化チタンコート膜が設けられたフィルムのサンシャインウェザーメーターの曝露試験における可視光線透過率の変化を示すグラフである。

【図24】実施例14で得られた有機-無機複合膜におけるスパッタリング時間と炭素原子およびケイ素原子の含有率との関係を示すグラフである。

【図25】実施例15で得られた有機-無機複合膜におけるスパッタリング時間と炭素原子およびケイ素原子の含有率との関係を示すグラフである。

【図26】実施例16で得られた有機-無機複合膜におけるスパッタリング時間と炭素原子およびケイ素原子の含有率との関係を示すグラフである。

【図27】実施例17で得られた有機-無機複合膜におけるスパッタリング時間と炭素原子およびケイ素原子の含有率との関係を示すグラフである。

【図28】実施例18で得られた有機-無機複合膜におけるスパッタリング時間と炭素原子およびケイ素原子の含有率との関係を示すグラフである。

【図29】実施例19で得られた有機-無機複合膜におけるスパッタリング時間と炭素原子およびケイ素原子の含有率との関係を示すグラフである。

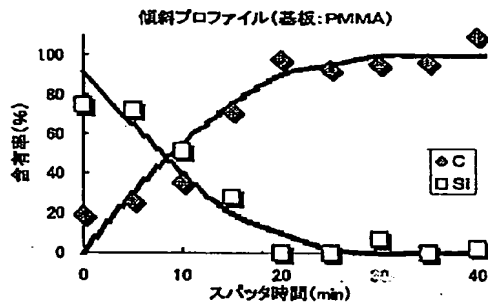
【図30】実施例21で得られた有機-無機複合膜におけるスパッタリング時間と炭素原子およびケイ素原子の含有率との関係を示すグラフである。

【図31】比較例9で得られた有機-無機複合膜におけるスパッタリング時間と炭素原子およびケイ素原子の含有率との関係を示すグラフである。

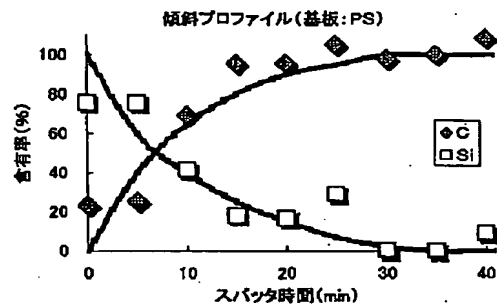
【図32】実施例24で得られた有機-無機複合膜におけるスパッタリング時間と炭素原子およびケイ素原子の含有率との関係を示すグラフである。

【図33】実施例25で得られた有機-無機複合膜におけるスパッタリング時間と炭素原子およびケイ素原子の含有率との関係を示すグラフである。

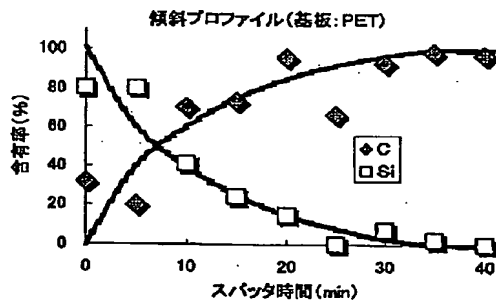
【図1】



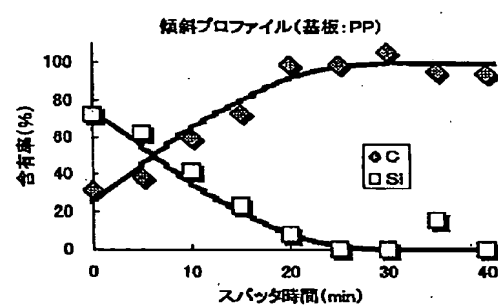
【図2】



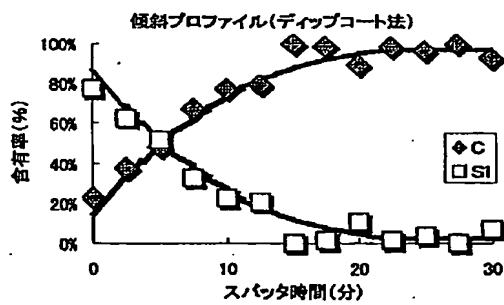
【図3】



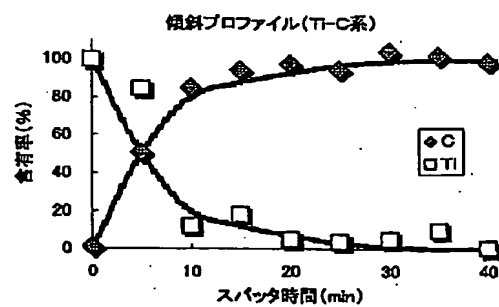
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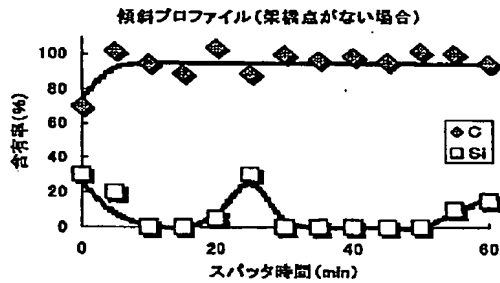
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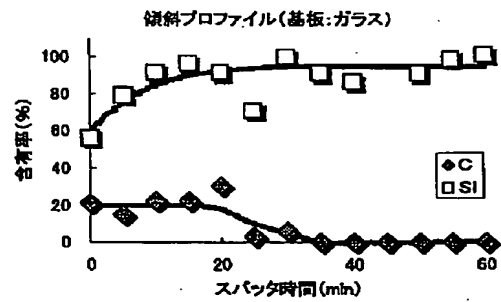
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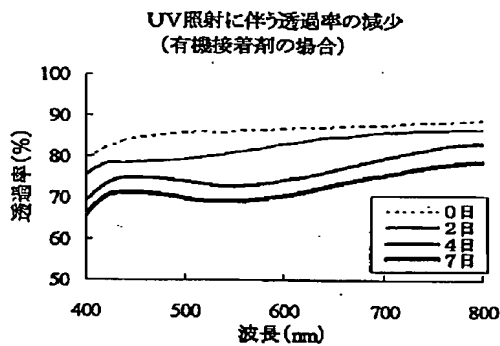
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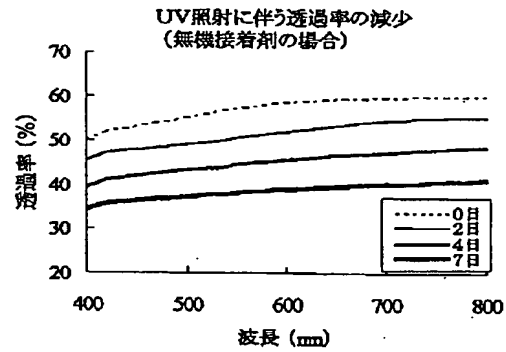
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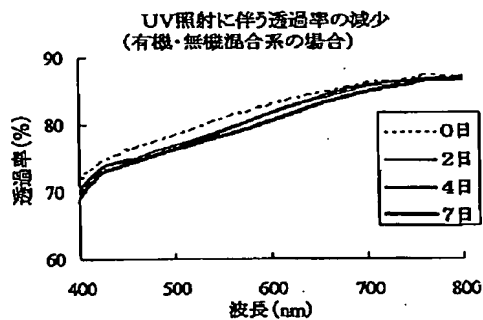
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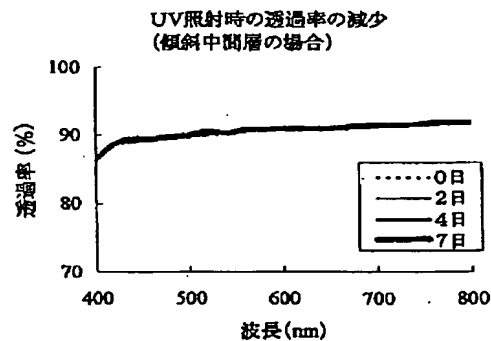
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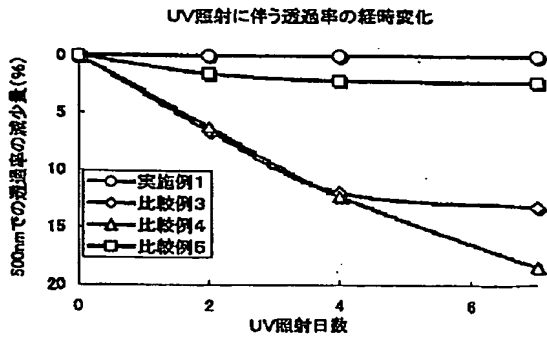
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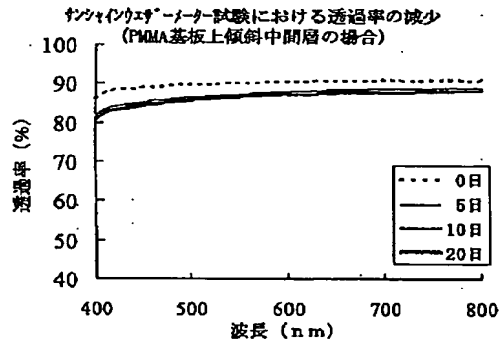
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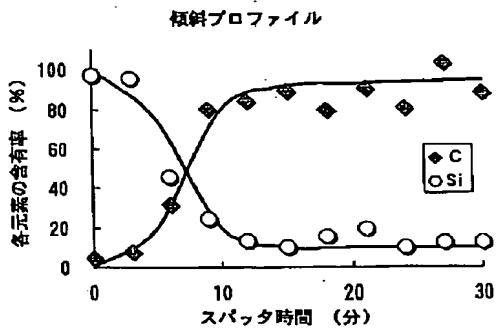
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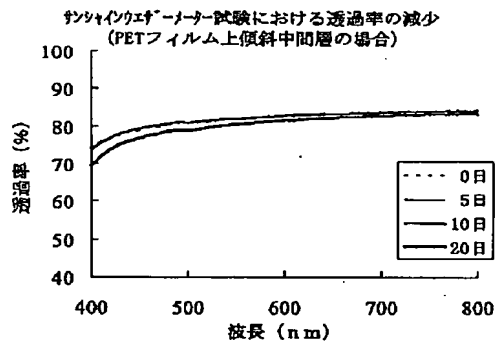
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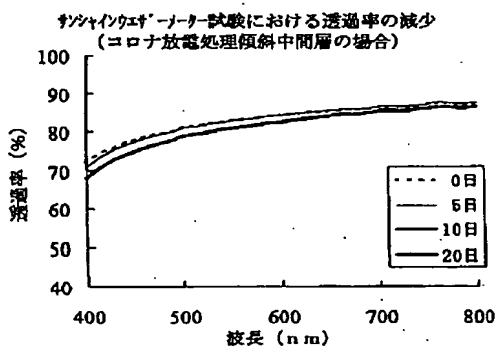
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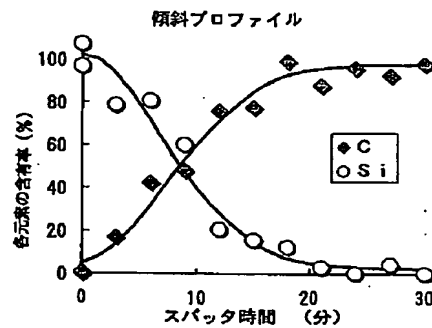
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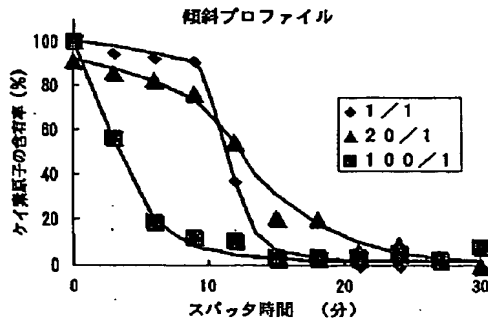
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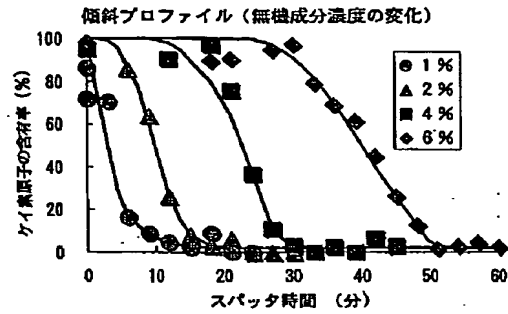
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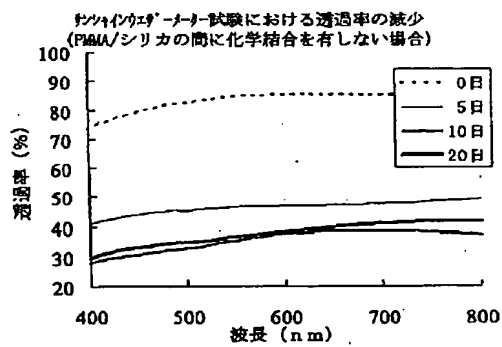
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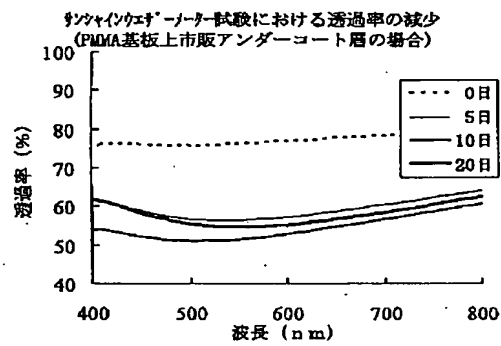
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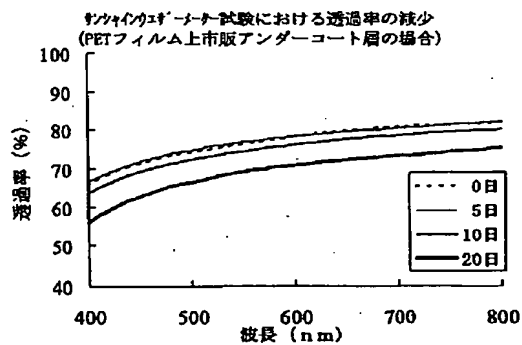
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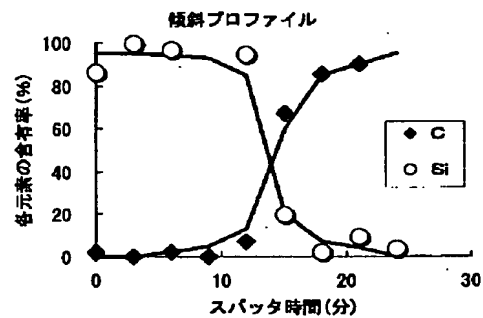
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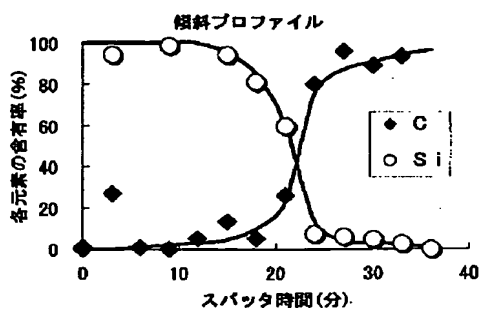
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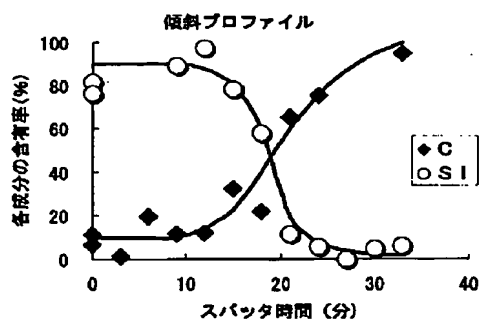
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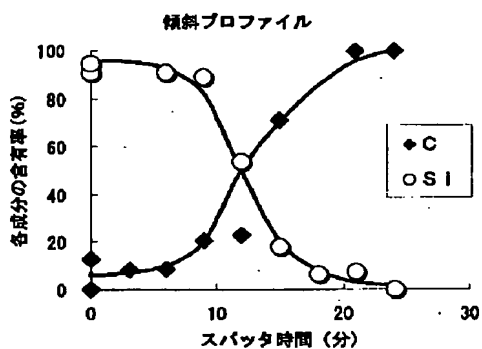
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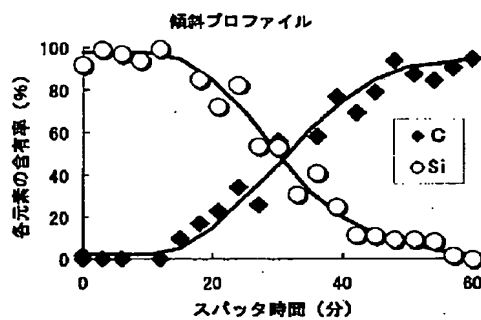
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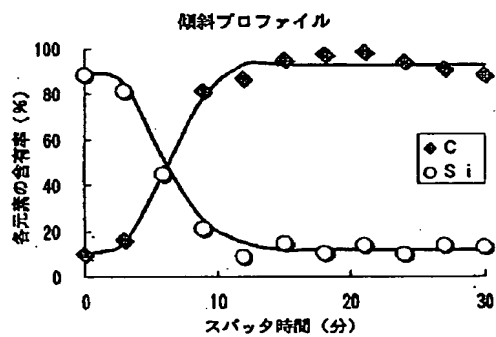
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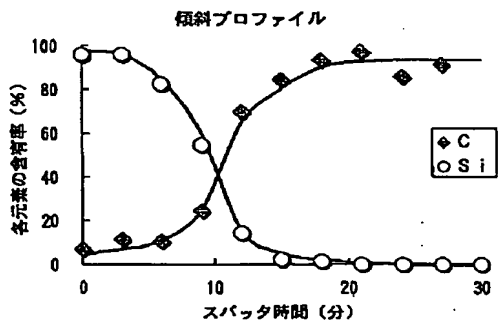
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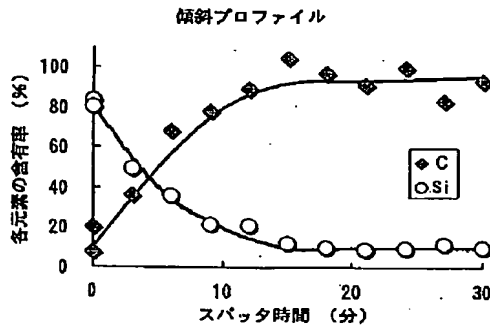
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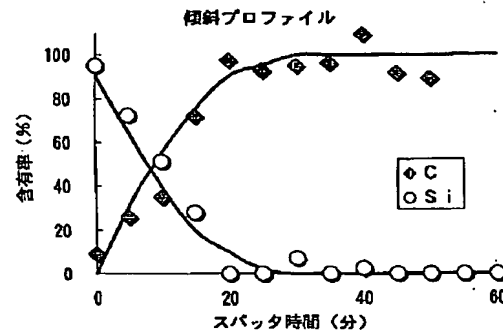
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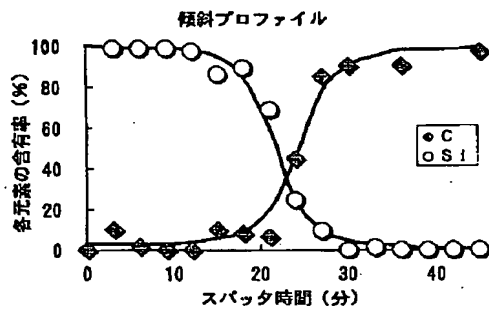
【図31】



【図32】



【図33】



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